

**COMPUTER CALCULATED PHASE DIAGRAMS FOR THE
Ni-W-Al, Ni-Al-Hf, Ni-Cr-Hf AND Co (Cr, Ni)-Ta-C SYSTEMS**

by L. Kaufman and H. Nesor

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MANLABS, INC.

21 ERIE STREET
CAMBRIDGE
MASS. 02139
TEL. (617) 491-2900

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ABSTRACT

Computer analysis of the W-Ni, W-Al, Ni-Al, Co-C, Ta-Co, Ta-C, Ta-Ni, Ta-Cr, Hf-Ni, Hf-Al, Hf-Cr, Al-W-Ni, Co-Ta-C, Al-Ni-Hf and Hf-Cr-Ni systems has been carried out in order to predict the isothermal sections and liquidus projections for these systems. The present results indicate that the Al-W-Ni and Hf-Cr-Ni systems offer opportunities for the growth of in-situ composites by means of controlled solidification, while the Al-Ni-Hf system suffers from low melting ternary eutectics. Calculation of the temperature and composition of the Co-TaC eutectic results in reasonable agreement with experimental observations and has been extended to consider effects of nickel and chromium additions on the eutectic temperature and composition.

I. INTRODUCTION AND SUMMARY

Controlled directional solidification techniques have been employed to produce in-situ composites of superalloys which offer outstanding combinations of high strength and high temperature stability. Such combinations of properties are required to meet needs for future generations of gas turbines.

The requirements for such materials have led to the exploration of multi-component alloys which promise to provide additional increments of strength and stability. Unfortunately, phase diagram data for such multi-component systems is generally not available. Such data is indispensable in determining whether or not a specific candidate alloy can be fabricated by means of controlled solidification and whether or not it will be stable in a desirable structure at elevated temperatures. In order to bridge this gap and provide guidance for experimental studies, computer based methods have been developed for calculating ternary phase diagrams (1-8)*. These methods can be applied to multi-component four and five component systems in special cases. The calculations provide complete descriptions of phase diagrams and thermochemical data and can be used to provide a wide variety of information on phase stability and transformations.

These techniques have been applied to calculate the following binary systems which are components of the systems of current interest:

- | | | |
|---------|----------|-----------|
| 1. W-Ni | 4. Ta-Co | 7. Ta-Cr |
| 2. W-Al | 5. Ta-C | 8. Hf-Ni |
| 3. Co-C | 6. Ta-Ni | 9. Hf-Al |
| | | 10. Hf-Cr |

The descriptions of these binary systems were combined with previous analyses of the Cr-Ni (4), Co-Cr (4), Co-Ni (4), Ni-C (6), Cr-C (6) and Ni-Al (8) systems to calculate significant

*Underscored numbers in parentheses denote references.

numbers of isothermal sections in the Al-W-Ni, Co-Ta-C, Al-Ni-Hf and Hf-Cr-Ni systems. These sections were employed to construct liquidus projections and melting trajectories for these ternary cases. In addition, the effects of Cr and Ni on the Co-TaC eutectic were calculated.

The present results indicate that the Al-W-Ni and Hf-Cr-Ni systems offer opportunities for the growth of in-situ composites while the Al-Ni-Hf systems suffers from low melting ternary eutectics. Calculation of the Co-TaC eutectic results in reasonable agreement with experiments while the computed effects of nickel and chromium additions up to 25% nickel and 20% chromium are found to be small.

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II. GENERAL BACKGROUND AND ANALYSIS OF BINARY SYSTEMS

Previous analyses of metallic systems (1,2) have made extensive use of symmetrical functions to describe the excess free energy of mixing. However, the complex nature of the current systems of interest requires that more general forms be considered along the lines presented in Equations 209-212 of Reference 1 and in References 3 and 4. Accordingly, the excess free energy of solution phases will be described by Equation 1 for the i-j system, where x is the atomic fraction of j,

$$F_E = x(1-x)[(1-x)g[T] + xh[T]] \quad (1)$$

where $g[T]$ and $h[T]$ are temperature dependent functions. Thus (1), the excess partial free energies of components i and j are given by Equations 2 and 3 as

$$\bar{F}_{Ei} = x^2[g[T] + (2x-1)(h[T] - g[T])] \quad (2)$$

and

$$\bar{F}_{Ej} = (1-x)^2[g[T] + 2x(h[T] - g[T])] \quad (3)$$

when $g[T] \equiv h[T]$, the excess free energy is symmetrical; when $g[T] = h[T] = \text{constant}$, the solution is regular. When $g[T] = h[T] = 0$ the solution is ideal.

Two descriptions have been employed for $g[T]$ (and $h[T]$). The simplest consists of the approximation

$$g[T] = g_0 + g_1T \quad (4)$$

where g_0 and g_1 are constants. Equation 4 is employed over a limited temperature range well removed from the third law range. On the other hand, description of $g[T]$ over a wider temperature range inclusive of 0°K requires the form of Equation 5

$$g[T] = g_2 + g_3T^2 + g_4T^3 \quad (5)$$

where g_2 , g_3 and g_4 are constants (3,4).

These generalized solution equations have been applied successfully to analyze a wide variety of the binary components of ternary systems (3-9). In the cases of present interest (which

are summarized in Tables 1-11) the value of $g[T]$ is listed first and $h[T]$ second for a given solution phase. Thus, reference to Table 1 shows that the excess free energy of the liquid phase in the W-Ni system is approximated as

$$F_E^L = x(1-x)[(1-x)(9400) + x(-7600 + 5.0T)] \text{ cal/g.at.} \quad (6)$$

where x is the atomic fraction nickel.

The free energy of the $W\text{Ni}_4$ compound phase is approximated by

$$F[W\text{Ni}_4] = (1-x_*)F_W^\theta + x_*F_{\text{Ni}}^\theta + x_*(1-x_*)[x_*^{-1}(1-x_*)^{-1}F_E^L[x_*] - C] \quad (7)$$

where $x_* = 0.8$ (i.e. the atom fraction nickel) for $W\text{Ni}_4$, θ is the base phase (i.e. fcc from Table 1), $F_E^L[x_*]$ is the numerical value of F_E^L in Equation 6 evaluated at $x = 0.8$, and C is the compound parameter (i.e. $520 + 5.45T$ in Table 1). Thus, definition of $g[T]$, $h[T]$, the compound parameter and base phases of the solution and compound phases in question is sufficient to define the thermochemical properties and binary phase diagrams of the systems of interest. The additional important factor which requires definition is the lattice stability of the pure components. These terms, relating the difference in free energy between bcc, hcp, fcc and liquid forms of the pure metals of interest, have been previously defined (1,3,4). Thus, the descriptions of the binary systems contained in Tables 1-11 generate the calculated phase diagrams shown in Figures 1-11. These diagrams are consistent with the observed binary phase diagrams (10-12) and collated thermochemical properties (13,14) which are limited or absent for the systems of interest.

The W-Ni case shown in Table 1 and Figure 1 requires definition of the solution and compound phase parameters for the fcc, bcc and liquid phases for the temperature range 300°K-3600°K as well as the compound $W\text{Ni}_4$ for the 300°K-1700°K range. Limited thermochemical data (15,16) are available for comparison. As a consequence, it is advisable to use a simple description of the excess free energy functions for the solution phases. Consequently, while the phase diagram in Figure 1 (which is directly calculated

from the parameters in Table 1) reproduces the general features of the observed phase diagram (10-12), some details are slightly distorted. In particular, the calculated diagram shows a peritectic at 1770°K between the liquid, bcc and fcc phases at nickel concentrations of 84, 1 and 82 atomic percent respectively. By contrast, the observed diagram shows a slight maximum in the fcc/liquid equilibrium (10) at 1783°K and 85 atomic percent nickel followed by a eutectic at 1773°K between the liquid, bcc and fcc phases at nickel concentrations of 79.3, 0.9 and 82.5 atomic percent respectively. Although such a configuration could be generated by calculation, it would require a more complex solution model than is justified by the meager thermochemical data presently available for the system. Table 1 compares limited experimental thermochemical data (15,16) with calculations based on the current description.

The W-Al system is described in Table 2 and Figure 2. Thermochemical data for this system could not be located for comparison with the present symmetrical description of the bcc and liquid phases. The calculated phase diagram is in good agreement with observed phase diagram data (10-12).

The current description of the Ni-Al system shown in Table 3 and Figure 3 has been presented in an earlier analysis of superalloy systems (8). The calculated and observed (10-12) phase diagram and thermochemical data (14) are in good agreement over the temperature and composition range of interest.

The description of the fcc and liquid phases of the Co-C system displayed in Table 4 provides a calculated phase diagram which is shown in Figure 4 and agrees with the observed phase diagram data (10-12) and limited thermochemical data (17) for this system. Analyses of the Ni-C and Cr-C systems have been presented (6). In line with the description of these systems, the excess free energy of the graphitic phase is characterized by a regular solution parameter of 10,000 cal/g.at.

Table 5 and Figure 5 show the results obtained for the Ta-Co system. The calculated results compare favorably with limi-

ted experimental thermochemical (18) and phase diagram data (10-12, 19).

The description of the Ta-C system shown in Table 6 and Figure 6 yields good agreement with recent thermochemical measurements of Kulkarni and Worrell (21) and experimental phase diagram data (10-12, 20).

The current description of the Ta-Ni system displayed in Table 7 reproduces the experimental phase diagram (10-12) quite adequately. The only difference between the diagram shown in Figure 7 and experimental results is that the former suggests a more extensive bcc field below 2000°K than the latter. No experimental thermochemical data could be located for this system which could be compared with the computed properties.

The description of the Ta-Cr system shown in Table 8 is in good agreement with experimental thermochemical observations (22) and generates the calculated phase diagram shown in Figure 8 which compares favorably with experimental findings (10-12, 19).

The limited experimental data on the Hf-Ni system are in conflict concerning the phase relations in the hafnium rich portion. The present description, shown in Table 9, generates the phase diagram of Figure 9 which provides a reasonable compromise between the conflicting experimental results (11, 23). This description suggests rather large negative free energies of formation for Hf-Ni compounds. Thus, the predicted free energy of formation of HfNi_5 is negative enough to reduce HfC so that the reaction shown in Equation 8 would be expected to proceed to the right at 1500°K



The free energy of formation of HfC near 1500°K is -24,300 cal/g.at. (14) while Table 9 shows that the free energy of formation of HfNi_5 is -10,075 cal/g.at. at this temperature; thus, the net free energy change for the reaction described by Equation 8 is nearly -1700 cal/g.at., favoring the reduction of HfC .

This reaction has been observed by Botic, Spencer and

Stuhrke (24) who made diffusion couples of HfC and Ni and observed formation of HfNi_5 in the interface after exposure near 1500°K. Their results support the present description of the Hf-Ni system shown in Table 9.

Tables 10 and 11 show the current description of the Hf-Al and Hf-Cr systems. No thermochemical data could be located for comparison with the computed properties. The phase diagrams generated by these representations, which are shown in Figures 10 and 11, are in good agreement with experimental phase diagrams (10-12,20) for these systems. The current description of the HfCr_2 Laves phase differs slightly from that employed recently (6) in order to obtain a closer conformity with experimentally deduced phase relations (20).

In addition to the above mentioned group of binary systems, analytical characterization of the Co-Cr, Co-Ni and Cr-Ni systems is required to perform the analysis of the multi-component systems of interest. However, these systems have been considered in detail in an earlier study (4).

Extension of the description of asymmetric binary phases into ternary systems has been detailed on the basis described earlier (3-9). Thus, the ternary analog of Equation 1 formulates the excess free energy of a ternary alloy with x atom fraction of tungsten, y atom fraction of nickel and 1-x-y atom fraction of aluminum as being equal to

$$x(1-x-y)(1-y)^{-1}((1-x-y)g[T]+xh[T])+y(1-x-y)(1-x)^{-1}((1-x-y)\ell[T]+ym[T] \\ +xy(x+y)^{-1}(xn[T]+yp[T]))$$

where $g[T]$ and $h[T]$ refer to the Al-W system, $\ell[T]$ and $m[T]$ refer to the Al-Ni system and $n[T]$ and $p[T]$ refer to the W-Ni system.

The free energy of the ternary compound phases in the systems of interest is formulated along the lines of Equations 291 and 292 of Reference 1, allowing for the variation in compound stoichiometry (3,4). Hence, consideration of a compound ψ with a base θ which runs between $i_{(1-x_*^1)}j_{x_*^1}$ and $j_{x_*^k}(1-x_*)$ and having a

general composition $i_{z_{\psi}}^j x_{\psi}^k (1-x_{\psi}-z_{\psi})$ is defined as follows.

$$p = (x_{*}^1 - x_{*}^1) / (1 - x_{*})$$

$$x_{\psi} = x_{*}^1 + y_{\psi} p, \quad z_{\psi} = 1 - x_{*}^1 - y_{\psi} (1 + p), \quad y_{\psi} = 1 - x_{\psi} - z_{\psi} \quad (9)$$

Thus, the free energy of the compound ψ is

$$F^{\psi} = z_{\psi} F_i^{\theta} + x_{\psi} F_j^{\theta} + y_{\psi} F_k^{\theta} + (1 - (y_{\psi}/x_{\psi})) \Delta F_A + (y_{\psi}/(1 - x_{\psi})) \Delta F_B + RT(y_{\psi} \ln y_{\psi} + z_{\psi} \ln z_{\psi} - (1 - x_{\psi}) \ln(1 - x_{\psi})) \quad (10)$$

where

$$\Delta F_A = x_{*}^1 (1 - x_{*}^1) [(1 - x_{*}^1) L_{ij} - x_{*}^1 L_{ij} - C_{ij}^{\psi}] \text{ cal/g.at.} \quad (11)$$

and

$$\Delta F_B = x_{*} (1 - x_{*}) [x_{*} L_{jk} + (1 - x_{*}) L_{kj} - C_{jk}^{\psi}] \text{ cal/g.at.} \quad (12)$$

where the L and C values in Equations 11 and 12 are defined for the component binary systems. These equations permit calculation of all compound/solution phase interactions. The solution phase interactions are carried out along the lines indicated earlier (1) on a pairwise basis. After each pairwise calculation has been completed, the results are combined to yield the most stable configuration.

Subsequent sections of this report detail the application of the present analyses to calculation of isothermal sections and liquidus projections in the Al-W-Ni, Co-Ta-C, Al-Ni-Hf and Hf-Cr-Ni systems. In addition, the effects of additions of Ni and Cr on the Co-TaC eutectic are considered.

III. ANALYSIS OF THE Al-W-Ni SYSTEM

The descriptions of the binary systems W-Ni, W-Al and Ni-Al presented in Section II were employed to calculate isothermal sections in the Al-W-Ni system. The only additional specification required to perform this analysis is definition of the compound parameters of counterphases for the compounds which are stable in the component binary systems. These parameters are listed in Table 12 and are set equal to zero in all cases except for the Ni_3Al - W_3Al pair. In this case a value of $C = -30,000$ was chosen to provide suitable agreement with the limited experimental results available.

Figures 12-16 display the results obtained for the calculated isothermal sections at 2000°K , 1800°K , 1700°K , 1600°K , 1400°K and 1200°K . In addition, Figure 12 provides a liquidus projection which shows that the minimum melting point is 1640°K for a composition corresponding to 73Ni-23Al-4W. Reference to Figures 12 and 13 shows that this minimum melting temperature corresponds to a 1640°K eutectic between the liquid phase, a bcc phase based on "NiAl", a fcc phase based on nickel and a bcc phase based on tungsten. The predominant solid phase at this point is the fcc solid solution. At temperatures just below the eutectic, the bcc phases dissolve in the fcc solid solution and the Ni_3Al phase, ξ , precipitates so that at 1600°K the 73Ni-23Al-4W alloy is largely fcc with a small amount of Ni_3Al precipitated (i.e. it lies in the two phase fcc + Ni_3Al field near the $\alpha+\xi/\alpha$ phase boundary at 1600°K). Figure 13 shows the calculated 1700°K and 1600°K sections along with an experimental section at 1473°K (25,26).

As the temperature is reduced further, the calculated sections shown in Figure 14 indicate that the 73-23-4 alloy enters the three phase field consisting of Ni_3Al , a nickel base fcc solid solution and a tungsten base bcc solid solution. This result differs from the observed 1073°K section shown in Figure 14 which suggests that the fcc (α) solid solution intrudes between the Ni_3Al and tungsten base phases. Figures 15 and 16 show a conversion of

the calculated sections into weight percentages of Ni, Al and W and temperatures in °F. The foregoing minimum melting conditions correspond to 76 w/o Ni-11 w/o Al-13 w/o W. Figures 14 (1400°K section) and 16 (2060°F) show that the minimum melting composition lies in the three phase fcc-Ni₃Al bcc (W) field. This composition lies very near the join between Ni₃Al and 97 a/o W-3 a/o Al.

The liquidus projections in Figures 12 and 15 show the fcc (α)/bcc (β)/Liquid trajectory which emanates from the W-Ni edge in the direction of the minimum melting composition. The discussion of the W-Ni binary system presented in Section II noted that the $\alpha/\beta/L$ reaction at 1770°K is calculated as a peritectic with the liquid composition at 84 a/o Ni. By contrast, the experimental reaction at 1773°K is reported to be a eutectic with the liquid composition at 79.3 a/o Ni. The liquidus projection in Figure 12 reflects the calculated 84 a/o Ni-16 a/o W value for the $\alpha/\beta/L$ trajectory. Experiments which are designed to grow tungsten fibers in a nickel base matrix along this $\alpha/\beta/L$ trajectory should allow for this difference in composition (i.e. 84 Ni-16 W vs. 79.3 Ni-20.7 W).

Thus, the present calculations suggest that the Al-W-Ni system is an attractive candidate for in-situ composite formation via controlled solidification.

IV. CALCULATION OF THE EFFECTS OF Ni AND Cr ADDITIONS ON THE Co-TaC EUTECTIC

Since the Co-TaC eutectic offers attractive opportunities for in-situ composite formation, nickel and chromium additions have been considered as a means of altering the properties of the cobalt matrix phase. Accordingly, calculation of the Co-TaC eutectic temperature and composition have been performed. In addition, an approximate method which has been developed and applied to the (Fe-Ni-Cr) vs. TiC system (9) has been used to estimate the effects of nickel and chromium additions on the Co-TaC eutectic.

The analyses of the Co-C, Ta-Co and Ta-C systems presented in Section II and the definition of the Co-Ta-C counterphases given in Table 12 permit calculation of the fcc-Liquid, TaC-Liquid and Ta_2C -Liquid phase boundaries shown in Figure 17. The isotherms at 1800°K, 2800°K, 3400°K and 4000°K disclose the boundary of the L + TaC field along the Co-TaC join which forms the quasi-binary section shown in Figure 18. The 1700°K section shown in the expanded view of Figure 17 provides a view just above the Co-TaC eutectic which is calculated to occur at 1680°K. Here the calculated eutectic composition is 0.932 Co-0.068 $Ta_{0.5}C_{0.5}$. The solubility of tantalum and carbon in cobalt is computed at 0.982 Co-0.018 $Ta_{0.5}C_{0.5}$. Table 14 lists these calculated results with temperature in °K and °F and compositions in atomic percent $Ta_{0.5}C_{0.5}$, atomic percent Ta and C, weight percent $Ta_{0.5}C_{0.5}$ and weight percent Ta and C. The latter are listed as the results of the exact calculation and compared with the experimental findings of Bibring and Seibel (27) who placed the eutectic temperature at 1675°K in excellent agreement with the present calculated results. In addition, Bibring and Seibel place the eutectic composition at 13.0 w/o TaC while the calculated result is 10.7 w/o TaC.

Calculation of an isothermal section for a five component system Co, Ni, Cr-TaC is beyond the range of current methods. However an approximate calculation of Figure 18 can be carried out along the lines presented earlier (9). This method depends on the

following conditions:

- a) The compound (i.e. TaC in this case) must be far more stable than any other compound in the five component system.
- b) The solubility of matrix components in the compound phase should be nil.
- c) The solubility of compound phase components in the matrix phase should be nil.

In the present case, condition (a) is met by the binary compounds in all of the ten systems which can be composed of the five elements in question. Condition (b) is met by nickel and cobalt but not by chromium, which dissolves in TaC. Condition (c) is met since TaC is only slightly soluble in Co as can be seen in Figure 18. The solubility of "TaC" in nickel is probably of comparable value, while the solubility of "TaC" in chromium may be slightly larger than either of the foregoing. The analytical description of these conditions can be defined precisely by considering the equilibrium between a liquid containing Co, Cr, Ni, Ta and C and $Ta_{0.50}C_{0.50}$ on the one hand and the same liquid and a solid Co, Cr, Ni alloy on the other hand. If x is the atom fraction of carbon, y the atom fraction of tantalum, u the atom fraction of nickel and v the atom fraction of chromium, then

$$y = (1-x_*)q, \quad x = x_*q, \quad u = u_0(1-q), \quad \text{and} \quad v = v_0(1-q) \quad (13)$$

where x_* is the atomic fraction of carbon in $Ta_{0.50}C_{0.50}$ and q is the composition variable along the join between $Co_{(1-u_0-v_0)}Ni_{u_0}Cr_{v_0}$. Thus in Figure 18 $u_0 = v_0 = 0$ and q represents the fraction of $Ti_{0.50}C_{0.50}$ at the boundary of the liquid field. If q_1 is the liquid boundary in equilibrium with the iron-rich phase and q_2 is the liquid boundary in equilibrium with $Ta_{0.50}C_{0.50}(\sigma)$ then

$$q_1 = q_2 = q_E \quad \text{when} \quad T = T_E \quad (14)$$

The remaining constraints required to obtain an approximate solution are that we can neglect the solubility of cobalt,

nickel and chromium in TaC and tantalum and carbon in $\text{Co}_{(1-u_o-v_o)}\text{Ni}_{u_o}\text{Cr}_{v_o}$. The errors introduced by assuming the validity of both these constraints will be discussed after presentation of the results of this computation.

Under these circumstances, the free energy of the five-component liquid is given by Equation 15 as

$$F^L = (1-q)[F_1 + E_1] + q[F_2 + E_2] + RT(q \ln q + (1-q) \ln(1-q)) \quad (15)$$

$$+ q(1-q)[E_3 - E_2 - E_1]$$

where

$$F_1 = (1-u_o-v_o)F_{\text{Co}}^L + u_o F_{\text{Ni}}^L + v_o F_{\text{Cr}}^L \quad (16)$$

$$+ RT[(1-u_o-v_o) \ln(1-u_o-v_o) + u_o \ln u_o + v_o \ln v_o]$$

$$F_2 = x_* F_{\text{C}}^L + (1-x_*) F_{\text{Ta}}^L + RT[(1-x_*) \ln(1-x_*) + x_* \ln x_*] \quad (17)$$

$$E_1 = u_o(1-u_o-v_o)L_{\text{Co-Ni}} + v_o(1-u_o-v_o)L_{\text{Co-Cr}} + u_o v_o L_{\text{Ni-Cr}} \quad (18)$$

$$E_2 = x_*(1-x_*)L_{\text{C-Ta}} \quad (19)$$

and

$$E_3 = x_*(1-u_o-v_o)L_{\text{Co-C}} + (1-u_o-v_o)(1-x_*)L_{\text{Co-Ti}} + u_o x_* L_{\text{C-Ni}} \quad (20)$$

$$+ v_o x_* L_{\text{C-Cr}} + u_o(1-x_*)L_{\text{Ta-Ni}} + v_o(1-x_*)L_{\text{Ta-Cr}}$$

In these equations F_{Co}^L , F_{Ni}^L , F_{Cr}^L , F_{C}^L and F_{Ta}^L are the free energies of the liquid forms of pure Co, Ni, Cr, C and Ta. The L parameters are the regular solution interaction parameters for the liquid phase in the binary systems designated. Thus, Reference 6, Table 6 and Reference 4 indicate that $L_{\text{C-Cr}} = -33,000$, $L_{\text{C-Ta}} = -22,200 - 5.0T$, $L_{\text{Co-Cr}} = -2,000$ and $L_{\text{Ni-Cr}} = -2,000$ cal/g.at. respectively. In addition, Table 5, Reference 4, and Table 4 respectively show that $L_{\text{Co-Ta}} = -20,000$, $L_{\text{Co-Ni}} = +800$ and $L_{\text{Co-C}} = -22,600 + 6.0T$. In the remaining cases, Table 8, Reference 6, and Table 7 show that $L_{\text{Ta-Cr}}$, $L_{\text{Ni-C}}$ and $L_{\text{Ta-Ni}}$ are not symmetrical. In these cases the most appropriate L value is that nearest the major component, i.e. Ta in Ta-Cr, C in Ni-C and Ta in Ta-Ni. Thus,

Equation 14 is an explicit function of q and T .

In similar fashion the free energy of $\text{Co}_{(1-u_o-v_o)}\text{Ni}_{u_o}\text{Cr}_{v_o}$ is given by

$$\begin{aligned} F^\phi = & (1-u_o-v_o)F_{\text{Fe}}^\phi + u_o F_{\text{Ni}}^\phi + v_o F_{\text{Cr}}^\phi - u_o(1-u_o-v_o)\phi_{\text{Co-Ni}} \\ & + v_o(1-u_o-v_o)\phi_{\text{Co-Cr}} + u_o v_o \phi_{\text{Ni-Cr}} \\ & + RT((1-u_o v_o) \ln(1-u_o v_o) + u_o \ln u_o + v_o \ln v_o) \end{aligned} \quad (21)$$

where ϕ is the stable form of the alloy $\text{Co}_{(1-u_o-v_o)}\text{Ni}_{u_o}\text{Cr}_{v_o}$ (i.e. bcc or fcc) at the temperature in question and $\phi_{\text{Co-Ni}}$, etc. is the interaction parameter of the ϕ phase in the binary system indicated. Finally, the free energy of the compound phase F^ψ is given by Equation 22 as

$$F^\psi = (1-x_*)F_{\text{Ta}}^\theta + x_* F_{\text{C}}^\theta + x_*(1-x_*)[L_{\text{C-Ti}} - C] \quad (22)$$

where $x_* = 0.50$, $\psi = \sigma$ and θ refers to the fcc base phase for the tantalum carbide phase as shown in Table 6. In the case at hand, $C = 116,300 - 10.32T$ cal/g.at.

The conditions for equilibrium can now be specified to define $q_1[T]$ and $q_2[T]$ by means of Equations 23 and 24

$$F^\phi = [F^L - q \partial F^L / \partial q] \text{ at } q = q_1 \quad (23)$$

and

$$F^\psi = [F^L + (1-q) \partial F^L / \partial q] \text{ at } q = q_2 \quad (24)$$

Substituting Equations 15-22 into Equations 23 and 24 yields the following explicit results

$$0 = RT \ln(1-q_1) + q_1^2 [E_3 - E_2 - E_1] + Q_1 \quad (25)$$

and

$$0 = RT \ln q_1 + (1-q_1)^2 [E_3 - E_2 - E_1] + Q_2 \quad (26)$$

where

$$\begin{aligned} Q_1 = & (1-u_o-v_o)\Delta F_{\text{Co}}^{\phi \rightarrow L} + u_o \Delta F_{\text{Ni}}^{\phi \rightarrow L} + v_o \Delta F_{\text{Cr}}^{\phi \rightarrow L} \\ & + u_o(1-u_o-v_o)(L_{\text{Co-Ni}} - \phi_{\text{Co-Ni}}) + v_o(1-u_o-v_o)(L_{\text{Co-Cr}} - \phi_{\text{Co-Cr}}) \\ & + u_o v_o (L_{\text{Ni-Cr}} - \phi_{\text{Ni-Cr}}) \end{aligned} \quad (27)$$

and

$$Q_2 = x_{\star} \Delta F_C^{\theta \rightarrow L} + (1-x_{\star}) \Delta F_{Ta}^{\theta \rightarrow L} + x_{\star}(1-x_{\star})C \\ + RT[x_{\star} \ln x_{\star} + (1-x_{\star}) \ln(1-x_{\star})] \quad (28)$$

Equations 25 and 26 can be solved explicitly for q_1 and q_2 at each temperature and the eutectic is located by applying Equation 14. Table 14 contains the results.

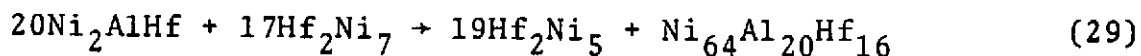
The second entry shows the value of T_E and q_E generated by the approximate solution for the case of $u_o = v_o = 0$. These values are to be compared with $T_E = 1680$, $q_E = 0.068$ shown in Figure 18. Thus, the approximate result yields a lower eutectic temperature and a slightly higher composition. Nevertheless, these values are still comparable with the experimental findings of Bibring and Seibel (27).

In the present case, the errors introduced by assuming zero solubility of Ta and C in cobalt and zero solubility in $Ta_{0.50}C_{0.50}$ do not appear to be important. This circumstance is probably due to the fact that the free energy of formation of tantalum carbide is much more negative than any other binary compounds in the systems of interest. The results in Table 14 are calculated with $\phi = \text{fcc}$ for cobalt and all of the alloys. The calculations indicate that the addition of nickel increases T_E and decreases q_E . Subsequent additions of chromium have little effect.

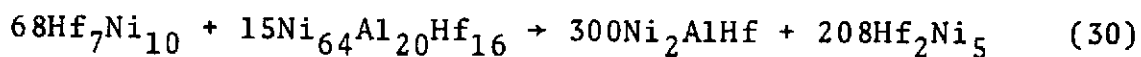
V. ANALYSIS OF THE Al-Ni-Hf SYSTEM

Recent successes have been achieved by addition of alloying elements to the Ni-Al system in order to generate quasi-binary eutectics between a high melting compound and Ni_3Al or the fcc-solid solution based on nickel. The present section and the succeeding section deal with analyses of the Al-Ni-Hf and Hf-Cr-Ni systems in order to investigate the stability of high melting eutectics in these systems which may provide the bases for new in-situ composites. Experimental data on the Al-Ni-Hf system is limited to one isothermal section at 1073°K. No experimental data for the Hf-Cr-Ni system could be located. Fortunately, the Al-Ni-Ti and Ti-Cr-Ni systems have been analyzed (7,8). These analyses provide a guide for the current calculations.

Table 13 describes the Al-Ni-Hf compound phase characterization employed in conjunction with the descriptions of Ni-Al, Hf-Ni and Hf-Al presented in Section II in order to compute the Al-Ni-Hf isothermal sections shown in Figures 19-23. Liquidus projections are displayed in Figures 19 and 22, while Figure 21 shows the observed isothermal sections due to Markiv and Bchnasheva (28). The latter includes the HfNi_3 phase which is not considered in the present study (i.e. see Figure 9 and Reference 11). The Al-Ni-Hf system contains two ternary compound phases in the composition range of interest. These are Ni_2AlHf and $\text{Ni}_{64}\text{Al}_{20}\text{Hf}_{16}$ (28). Table 15 provides a description of these compounds as well as the resultant calculated melting temperatures and free energies of formation. The base phase and compound parameter, C, for Ni_2AlHf were chosen to be the same as those determined for Ni_2AlTi (8). The compound parameter for $\text{Ni}_{64}\text{Al}_{20}\text{Hf}_{16}$ was estimated on the basis of the following observed reactions (28).



and



The equation displayed in Table 15 describes the free energy of the ternary compound (Ni_2AlHf and/or $\text{Ni}_{64}\text{Al}_{20}\text{Hf}$) as a function of temperature in terms of the base (θ), the compound parameter (C) and the interaction parameters (L_{ij} , etc.). The latter are given in Tables 3, 9 and 10 and permit explicit specification of the free energy of these phases. The calculated isothermal sections and liquidus projections in Figures 19-23 show a number of quasi-binary and ternary eutectic reactions. These are listed in Table 16 for convenience.

Examination of Figures 19-23 and Table 16 shows that the Al-Ni-Hf system is not likely to produce composites which are stable at high temperatures. This result is due to the stability of the liquid phase at 1500°K (2240°F) and 1400°K (2660°F).

VI. ANALYSIS OF THE Hf-Cr-Ni SYSTEM

The results obtained for the Hf-Cr-Ni system by synthesis of the Hf-Ni and Hf-Cr results shown in Section II and the Cr-Ni results published earlier (4) are contained in Figures 24-27 and Table 17. Experimental data concerning this ternary system could not be located. As a consequence, the present calculations have been guided by earlier results for the Ti-Cr-Ni system (7) which did not include ternary compound phases.

In contrast to the findings obtained for the Al-Ni-Hf system discussed earlier in Section V, the isothermal sections shown in Figures 24-27 indicate that the quasi-binary section Hf_2Ni_7 -59.5 a/o Ni/40.5 a/o Cr may provide opportunities for synthesis of an in-situ composite with high temperature stability since the calculated eutectic between Hf_2Ni_7 and the fcc nickel base solid solution 59.5 a/o Ni-40.5 a/o Cr is 1590°K or 2402°F.

The principal difference between the Hf-Cr-Ni case currently under discussion and the Al-Ni-Hf case described in Section V is the interaction between the liquid and Ni_7Hf_2 phases designated L and Y respectively. In the former Al-Ni-Hf case (Figure 19) the addition of aluminum to Ni-Hf increases the stability of the liquid phase relative to that of Ni_7Hf_2 (Y) so that the Y- α (fcc) interaction does not eliminate intrusion of the liquid phase until the temperature is reduced below 1400°K (i.e. see Figure 14). By contrast, reference to Figures 24 and 25 for the Hf-Cr-Ni case shows that the Y-L interaction moves rapidly across the ternary triangle so that it nearly reaches the Ni-Cr edge at 1600°K. The eutectic reaction at 1590°K yields Ni_7Hf_2 (Y) with very little chromium in a fcc matrix of 59.5 a/o Ni-40.5 a/o Cr (α). The ratio of Y/ α which forms from the 63 a/o Ni-35 a/o Cr-3 a/o Hf liquid is 0.135/0.865. Consequently, this combination should prove to be an excellent candidate for the formation of in-situ composites.

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TABLE 1
SUMMARY OF EXCESS FREE ENERGY AND
COMPOUND PARAMETERS FOR THE W-Ni SYSTEM
(cal/g.at., °K)

Liquid	9400 -7600 + 5.0T	FCC	10000 -7000 + 5.0T
BCC	15000 15000		

<u>Compound</u>	<u>x_*</u>	<u>Structure</u>	<u>Base</u>	<u>Compound Parameter</u>
W _{Ni} ₄	0.80	b.c. tetragonal	fcc	520 + 5.45T

Calculated Thermochemical Properties
of Compound Phase

<u>x_*</u>	<u>ΔH_f[300°K]</u>	<u>ΔS_f[300°K]</u>
0.80	-255	0.20

Comparison of Calculated and Observed
Thermochemical Properties

T = 1173°K Free Energy of Formation of W_{Ni}₄
-490 (cal/g.at.) (calc.); -1150 (cal/g.at.) (obs) (15)

T = 1173°K, fcc phase

<u>x</u> (at.fr.Ni)	<u>Activity of Nickel</u> (calc.) (obs.) (15)		<u>Activity of Tungsten</u> (calc.) (obs.) (15)	
0.90	0.86	0.83	0.46	0.14
0.92	0.89	0.87	0.32	0.08
0.93	0.91	0.88	0.26	0.07
0.95	0.94	0.91	0.15	0.04
0.97	0.97	0.95	0.08	0.02

T = 2000°K, Liquid Phase

0.80	0.78	0.60 (16)	0.46	0.40 (16)
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TABLE 2
SUMMARY OF EXCESS FREE ENERGY AND
COMPOUND PARAMETERS FOR THE W-Al SYSTEM
(cal/g.at., °K)

Liquid	-8000 + 6.25T	BCC	-5700 + 6.25T
	-8000 + 6.25T		-5700 + 6.25T

<u>Compound</u>	<u>x_*</u>	<u>Structure</u>	<u>Base</u>	<u>Compound Parameter</u>
WAl ₄	0.80	Monoclinic	fcc	7600 + 6.0T

Calculated Thermochemical Properties
of Compound Phase

<u>x_*</u>	<u>ΔH_f[300°K]</u>	<u>ΔS_f[300°K]</u>
0.80	-2000	-0.07

TABLE 3
SUMMARY OF EXCESS FREE ENERGY AND
COMPOUND PARAMETERS FOR THE Ni-Al SYSTEM (8)
(cal/g.at., °K)
(300°K ≤ T ≤ 2000°K)

Liquid	-48608	-	33.02T	+	$3.328 \times 10^{-2} T^2$	-	$6.528 \times 10^{-6} T^3$
	-22008	-	31.12T	+	$3.328 \times 10^{-2} T^2$	-	$6.528 \times 10^{-6} T^3$
FCC	-45408	-	35.72T	+	$3.328 \times 10^{-2} T^2$	-	$6.528 \times 10^{-6} T^3$
	-4758	-	43.62T	+	$3.328 \times 10^{-2} T^2$	-	$6.528 \times 10^{-6} T^3$
BCC	-52808	-	33.72T	+	$3.328 \times 10^{-2} T^2$	-	$6.528 \times 10^{-6} T^3$
	-67319	+	52.73T	-	$2.200 \times 10^{-2} T^2$	+	$4.316 \times 10^{-6} T^3$

<u>Compound</u>	<u>x*</u>	<u>Structure</u>	<u>Base</u>	<u>Compound Parameter</u>
Ni ₃ Al	0.250	AuCu ₃	fcc	7600 + 2.60T
Ni ₂ Al ₃	0.600	Trigonal	fcc	16500 - 5.15T
NiAl ₃	0.750	Orthorhombic	fcc	14000 - 6.10T

Comparison of Calculated and Observed
Thermochemical Properties

<u>x</u> (at.fr.Al)	<u>Phase</u>	<u>ΔH_f[300°K]*</u>		<u>ΔF_f(excess)[1273°K]*</u>	
		(calc)	(obs) (14)	(calc)	(obs) (14)
0.10	fcc	-3960	-3650 ± 1000	-4250	-3025 ± 2000
0.25	Ni ₃ Al	-9790	-9000 ± 1000	-10100	-8000 ± 2000
0.40	bcc	-12750	-12350 ± 1000	-----	-----
0.50	bcc	-13450	-14050 ± 1000	-9300	-11200 ± 2000
0.55	bcc	-13350	-14050 ± 1000	-----	-----
0.60	Ni ₂ Al ₃	-12450	-13500 ± 1000	-10250	-9000 ± 2000
0.75	NiAl ₃	-8500	-9000 ± 1000	-----	-----

*Based on fcc nickel and fcc aluminum.

TABLE 4
SUMMARY OF EXCESS FREE ENERGY AND
COMPOUND PARAMETERS FOR THE Co-C SYSTEM
(cal/g.at., °K)

Liquid	-22600 + 6.0T	FCC	-14300 - 2.63T
	-22600 + 6.0T		-22900 + 1.44T

TABLE 5
SUMMARY OF EXCESS FREE ENERGY AND
COMPOUND PARAMETERS FOR THE Ta-Co SYSTEM
(cal/g.at., °K)

Liquid	-20,000 ;	BCC	-1,000 ;	FCC	-13,500
	-20,000		-1,000		-13,500

<u>Compound</u>	<u>x*</u>	<u>Structure</u>	<u>Base</u>	<u>Compound Parameter</u>
Ta ₂ Co	0.333	CuAl ₂	bcc	8300
Ta ₇ Co ₆	0.461	W ₆ Fe ₇	fcc	16400
TaCo ₂	0.667	Laves Phase	hcp	14300

Comparison of Calculated and Observed (18)
Thermochemical Properties of Compound Phases

<u>x*</u>	<u>ΔH_f[300°K]</u>	<u>ΔS_f[300°K]</u>	<u>ΔF_f[1200°K]</u>
0.333	-5650 (calc)	+0.38 (calc)	-----
0.461	-8850 (calc)	-0.53 (calc)	-----
0.667	-7180 (calc)	-0.37 (calc)	-6740 (calc)
0.667	-----	-----	-6400 ± 300 (obs)(18)

TABLE 6
SUMMARY OF EXCESS FREE ENERGY AND
COMPOUND PARAMETERS FOR THE Ta-C SYSTEM
(cal/g.at., °K)

$$\Delta F_C^{\epsilon \rightarrow L} = -3.0T$$

Liquid	-22,200 - 5.0T	BCC	-37,200 - 5.0T
	-22,200 - 5.0T		-37,200 - 5.0T

<u>Compound</u>	<u>x_*</u>	<u>Structure</u>	<u>Base</u>	<u>Compound Parameter</u>
Ta ₂ C	0.333	Hexagonal	hcp	94,400 - 12.10T
TaC	0.500	NaCl	fcc	116,300 - 10.32T

Calculated and Observed (21)
Thermochemical Properties of Compound Phases

<u>x_*</u>	<u>ΔH_f[300°K]</u>	<u>ΔS_f[300°K]</u>
0.333	-15900 (calc)	-0.9 (calc)
	-15800 ± 700 (obs)(21)	-0.7 ± 0.2 (obs)(21)
0.500	-17000 (calc)	0.0 (calc)
	-17200 ± 1000 (obs)(21)	0.0 ± 0.2 (obs)(21)

TABLE 7
SUMMARY OF EXCESS FREE ENERGY AND
COMPOUND PARAMETERS FOR THE Ta-Ni SYSTEM
(cal/g.at., °K)

Liquid	-5000	FCC	-3900
	-25000		-23900
BCC	-7000		
	-7000		

<u>Compound</u>	<u>x_*</u>	<u>Structure</u>	<u>Base</u>	<u>Compound Parameter</u>
Ta ₂ Ni	0.333	bct (CuAl ₂)	bcc	9700
Ta ₇ Ni ₆	0.461	rhomb. (W ₆ Fe ₇)	fcc	10100 + 1.7T
TaNi ₂	0.667	bct (MoSi ₂)	bcc	9480 - 1.16T
TaNi ₃	0.750	orthorhom. (TiCu ₃)	fcc	12700

Calculated Thermochemical Properties
of Compound Phases

<u>x_*</u>	<u>ΔH_f[300°K]</u>	<u>ΔS_f[300°K]</u>
0.333	-4430	0.00
0.461	-4900	+0.11
0.667	-5550	-0.26
0.750	-5585	-0.21

TABLE 8
SUMMARY OF EXCESS FREE ENERGY AND
COMPOUND PARAMETERS FOR THE Ta-Cr SYSTEM
(cal/g.at., °K)

Liquid	-1700 +2000	BCC	+2200 +8800
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<u>Compound</u>	<u>x*</u>	<u>Structure</u>	<u>Base</u>	<u>Compound Parameter</u>
TaCr ₂	0.667	Laves Phase	hcp	18300 + 1.6T

Calculated and Observed (22)
Thermochemical Properties of Compound Phase

<u>x*</u>	<u>ΔH_f[300°K]</u>	<u>ΔS_f[300°K]</u>
0.667	-2200 (calc)	+0.10 (calc)
	-2200 ± 200 (obs)(22)	-0.07 ± 0.10 (obs)(22)

TABLE 9
SUMMARY OF EXCESS FREE ENERGY AND
COMPOUND PARAMETERS FOR THE Hf-Ni SYSTEM
(cal/g.at., °K)

Liquid	-40000 -70000	HCP	-16000 -46000
BCC	-15000 -45000	FCC	-18500 -48500

<u>Compound</u>	<u>x_*</u>	<u>Structure</u>	<u>Base</u>	<u>Compound Parameter</u>
Hf ₂ Ni	0.333	AlCu ₂	fcc	3400
HfNi	0.500	Orthorhombic	fcc	8700
Hf ₇ Ni ₁₀	0.588	Orthorhombic	fcc	5400
Hf ₂ Ni ₅	0.714	-----	fcc	6500
Hf ₂ Ni ₇	0.778	-----	fcc	10300
HfNi ₅	0.833	FCC(F $\bar{4}$ 3m)	fcc	8400

Calculated Thermochemical Properties
of Compound Phases

<u>x_*</u>	<u>ΔH_f [300°K]</u>	<u>ΔS_f [300°K]</u>
0.333	-11,330	0.0
0.500	-15,525	0.0
0.588	-14,945	0.0
0.714	-13,640	0.0
0.778	-12,540	0.0
0.833	-10,075	0.0

TABLE 10
SUMMARY OF EXCESS FREE ENERGY AND
COMPOUND PARAMETERS FOR THE Hf-Al SYSTEM
(cal/g.at., °K)

Liquid	-35000 -35000	HCP	-36400 -36400
BCC	-35400 -35400		

<u>Compound</u>	<u>x*</u>	<u>Structure</u>	<u>Base</u>	<u>Compound Parameter</u>
Hf ₃ Al	0.250	Ti ₃ Al	hcp	9,200
Hf ₂ Al	0.333	CuAl ₂	hcp	11,100
Hf ₃ Al ₂	0.400	Tetragonal	bcc	16,850 - 1.92T
Hf ₄ Al ₃	0.428	Hexagonal	bcc	16,970 - 1.78T
HfAl	0.500	Orthorhombic	bcc	17,700 - 1.64T
Hf ₂ Al ₃	0.600	Orthorhombic	bcc	21,380 - 2.35T
HfAl ₂	0.667	Laves	hcp	20,900
HfAl ₃	0.750	TiAl ₃	hcp	23,500

Calculated Thermochemical Properties
of Compound Phases

<u>x*</u>	<u>ΔH_f[300°K]</u>	<u>ΔS_f[300°K]</u>
0.250	-7950	0.11
0.333	-9800	0.14
0.400	-10400	0.60
0.428	-10600	0.57
0.500	-11060	0.62
0.600	-11350	0.49
0.667	-11540	0.29
0.750	-9990	0.32

TABLE 11
SUMMARY OF EXCESS FREE ENERGY AND
COMPOUND PARAMETERS FOR THE Hf-Cr SYSTEM
(cal/g.at., °K)

Liquid	0	HCP	9000
	0		9000
BCC	6000		
	6000		

<u>Compound</u>	<u>x_*</u>	<u>Structure</u>	<u>Base</u>	<u>Compound Parameter</u>
HfCr ₂	0.667	Laves Phase	hcp	7900 + 4.3T

Calculated Thermochemical Properties
of Compound Phase

<u>x_*</u>	<u>ΔH_f[300°K]</u>	<u>ΔS_f[300°K]</u>
0.667	-420	+0.95

TABLE 12
SUMMARY OF COMPOUND COUNTER PHASES
IN TERNARY SYSTEMS

<u>Compound</u>	<u>Base</u>	<u>Structure</u>	<u>Compound Parameter</u> (cal/g.at.)
<u>Al-W-Ni</u>			
Ni ₃ Al	fcc	AuCu ₃	7,600 + 2.60T
W ₃ Al	fcc	AuCu ₃	-30,000
Ni ₂ Al ₃	fcc	Trigonal	16,500 - 5.15T
Mo ₂ Al ₃	fcc	Trigonal	0
WNi ₄	fcc	b.c. Tetragonal	520 + 5.45T
AlNi ₄	fcc	b.c. Tetragonal	0
WAl ₄	fcc	Monoclinic	7,600 + 6.0T
NiAl ₄	fcc	Monoclinic	0
<u>Co-Ta-C</u>			
TaCo ₂	hcp	Laves Phase	14,300
CCo ₂	hcp	Laves Phase	0
Ta ₂ C	hcp	Hexagonal	94,400 - 12.10T
Co _{0.95} C _{0.05}	hcp	Hexagonal	0
TaC	fcc	NaCl	116,300 - 10.32T
Co _{0.95} C _{0.05}	fcc	NaCl	0

TABLE 13
SUMMARY OF COMPOUND COUNTER PHASES
IN TERNARY SYSTEMS

<u>Compound</u>	<u>Base</u>	<u>Structure</u>	<u>Compound Parameter</u> (cal/g.at.)
<u>Al-Ni-Hf</u>			
Ni ₃ Al	fcc	AuCu ₃	7,600 + 2.60T
Ni ₃ Hf	fcc	AuCu ₃	0
Ni ₂ Al ₃	fcc	Trigonal	16,500 - 5.15T
Hf ₂ Al ₃	fcc	Trigonal	0
Ni ₅ Hf	fcc	fcc ($\overline{F}43m$)	8,400
Ni ₅ Al	fcc	fcc ($\overline{F}43m$)	0
Ni ₇ Hf ₂	fcc	-----	10,300
Ni ₇ Al ₂	fcc	-----	0
HfAl ₂	hcp	Laves Phase	20,900
HfNi ₂	hcp	Laves Phase	0
HfAl ₃	hcp	TiAl ₃	23,500
HfNi ₃	hcp	TiAl ₃	0
<u>Hf-Cr-Ni</u>			
Ni ₅ Hf	fcc	fcc ($\overline{F}43m$)	8,400
Ni ₅ Cr	fcc	fcc ($\overline{F}43m$)	0
Ni ₇ Hf ₂	fcc	-----	10,300
Ni ₇ Cr ₂	fcc	-----	0
HfCr ₂	hcp	Laves Phase	7,900 + 4.3T
HfNi ₂	hcp	Laves Phase	0

TABLE 14

CALCULATED QUASI BINARY EUTECTIC CONDITIONS
BETWEEN Co-Ni-Cr ALLOYS AND TaC

Matrix Composition Atomic Percent Co-Ni-Cr Weight Percent (Co-Ni-Cr)	Eutectic Temperature		Eutectic Composition [Atomic Percent TaC/ Atomic Percent Co-Ni-Cr] [Atomic Percent Ta- Atomic Percent C/ Atomic Percent Co-Ni-Cr] (Weight Percent TaC/ Weight Percent Co-Ni-Cr) (Weight Percent Ta- Weight Percent C/ Weight Percent Co-Ni-Cr)
	°K	(°F)	
100-0-0	1680	(2564)	6.8/93.2-0-0
(100-0-0)	(Exact Calculation)		3.4-3.4/93.2-0-0
(observed) 1675°K(2555°F) -13.0/87.0-0-0			10.7/89.3-0-0
(H.Bibring and G. Seibel, Compt. Rend (1969) 268 144) (27)			10.0-0.7/89.3-0-0
100-0-0	1658	(2524)	6.1/93.9-0-0
(100-0-0)	(Approximate Calculation)		3.05-3.05/93.9-0-0
			9.6/90.4-0-0
			9.0-0.6/90.4-0-0
75-25-0	1694	(2589)	4.0/72.0-24.0-0
(75-25-0)	(Approximate Calculation)		2.0-2.0/72.0-24.0-0
			6.4/70.2-23.4-0
			6.0-0.4/70.2-23.4-0
70.9-23.6-5.5	1698	(2596)	4.1/68.0-22.6-5.3
(71.2-23.8-5.0)	(Approximate Calculation)		2.05-2.05/68.0-22.6-5.3
			6.6/66.6-22.2-4.6
			6.2-0.4/66.6-22.2-4.6
66.7-22.3-11.0	1697	(2595)	4.2/63.9-21.4-10.5
(67.5-22.5-10.0)	(Approximate Calculation)		2.1-2.1/63.9-21.4-10.5
			6.8/63.0-21.1-9.1
			6.4-0.4/63.0-21.1-9.1
62.6-20.9-16.5	1691	(2584)	4.2/60.0-20.0-15.8
(63.7-21.3-15.0)	(Approximate Calculation)		2.1-2.1/60.0-20.0-15.8
			6.8/59.5-19.8-13.9
			6.4-0.4/59.5-19.8-13.9
58.5-19.5-22.0	1680	(2564)	4.2/56.0-18.7-21.1
(60.0-20.0-20.0)	(Approximate Calculation)		2.1-2.1/56.0-18.7-21.1
			6.8/55.8-18.7-18.7
			6.4-0.4/55.8-18.7-18.7

TABLE 15
CALCULATED THERMOCHEMICAL PROPERTIES OF
TERNARY Al-Ni-Hf COMPOUNDS

<u>Compound</u>	<u>Calculated Melting Point</u>		<u>Base</u>	<u>Compound Parameter</u> (cal/g.at.)
	<u>°K</u>	<u>(°F)</u>		
Ni ₂ AlHf	1567	(2360)	bcc	7950
Ni ₆₄ Al ₂₀ Hf ₁₆	1430	(2115)	fcc	3700

Calculated Free Energy of Formation*
(cal/g.at.)

<u>T°K</u>	<u>Ni₂AlHf</u>	<u>Ni₆₄Al₂₀Hf₁₆</u>
1200	-17550	-15250
1000	-17850	-15700
500	-17950	-16100
300	-17600	-16050

$$\begin{aligned}
 F^{\psi} = & (1-x_{*}-y_{*})F_i^{\theta} + x_{*}F_j^{\theta} + y_{*}F_k^{\theta} + x_{*}(1-x_{*}-y_{*})(1-y_{*})^{-1}[(1-x_{*}-y_{*})L_{ij}+x_{*}L_{ji}-C] \\
 & + y_{*}(1-x_{*}-y_{*})(1-x_{*})^{-1}[(1-x_{*}-y_{*})L_{ik}+y_{*}L_{ki}-C] \\
 & + x_{*}y_{*}(x_{*}+y_{*})^{-1}[x_{*}L_{jk}+y_{*}L_{kj}-C] \text{ cal/g.at.}
 \end{aligned}$$

* from hcp Hf, fcc Ni and fcc Al.

TABLE 16
SUMMARY OF CALCULATED ISOTHERMAL
TRANSFORMATION CONDITIONS IN THE
Al-Ni-Hf SYSTEM

<u>Reaction Type</u>	<u>Phases Involved</u>	<u>Temperature</u>		<u>Composition</u>	
		°K	(°F)	Atomic Percent Ni-Al-Hf	Weight Percent Ni-Al-Hf
Quasibinary Eutectic	L/Ni ₂ AlHf + Ni ₆₄ Al ₂₀ Hf ₁₆	1390	(2042)	61-21-18	48.6-7.7-43.7
Quasibinary Eutectic	L/Ni ₃ Al + Ni ₆₄ Al ₂₀ Hf ₁₆	1330	(1934)	68-22-10	62.7-9.3-28.0
Quasibinary Eutectic	L/Ni ₇ Hf ₂ + Ni ₆₄ Al ₂₀ Hf ₁₆	1320	(1916)	68-14-18	52.6-5.0-42.4
Quasibinary Eutectic	L/Ni ₂ AlHf + Ni ₇ Hf	1300	(1880)	64-12-24	44.9-3.9-51.2
Quasibinary Eutectic	L/Ni ₇ Hf ₂ + Ni ₃ Al	1290	(1862)	76-14-10	67.3-5.7-27.0
Quasibinary Eutectic	L/Ni ₂ AlHf + bcc	1280	(1844)	57-35-8	58.5-16.4-25.0
Ternary Eutectic	L/Ni ₇ Hf ₂ + fcc + Ni ₃ Al	1280	(1844)	79-12-9	70.6-4.9-24.5
Ternary Eutectic	L/Ni ₇ Hf ₂ +Ni ₃ Al + Ni ₆₄ Al ₂₀ Hf ₁₆	1280	(1844)	74-15-11	64.8-6.0-29.2
Ternary Eutectic	L/Ni ₂ AlHf +bcc+Ni ₆₄ Al ₂₀ Hf ₁₆	1260	(1808)	60-32-8	60.5-14.9-24.6

TABLE 17
SUMMARY OF CALCULATED ISOTHERMAL
TRANSFORMATION CONDITIONS IN THE
Hf-Cr-Ni SYSTEM

<u>Reaction Type</u>	<u>Phases Involved</u>	<u>Temperature</u>		<u>Composition</u>	
		<u>°K</u>	<u>(°F)</u>	<u>Atomic Percent Ni-Cr-Hf</u>	<u>Weight Percent Ni-Cr-Hf</u>
Quasibinary Eutectic	L/Hf ₂ Ni ₇ + fcc	1590	(2402)	62-35-3	60.8-30.3-8.9
Quasibinary Eutectic	L/Hf ₂ Ni ₇ + Hf(Cr,Ni) ₂	1490		59-25-16	
Quasibinary Eutectic	L/Hf(Cr,Ni) ₂ + Ni ₅ Hf ₂	1460		63-8-29	
Ternary Eutectic	L/fcc + Hf(Cr,Ni) ₂ +Hf ₂ Ni ₇	1460	(2168)	52-43-5	49.4-36.2-14.4
Ternary Eutectic	L/Hf(Cr,Ni) ₂ + Hf ₂ Ni ₅ +Hf ₇ Ni ₁₀	1450		62-6-32	
Ternary Eutectic	L/Hf(Cr,Ni) ₂ +Hf ₂ Ni ₅ +Hf ₂ Ni ₇	1450		63-10-27	

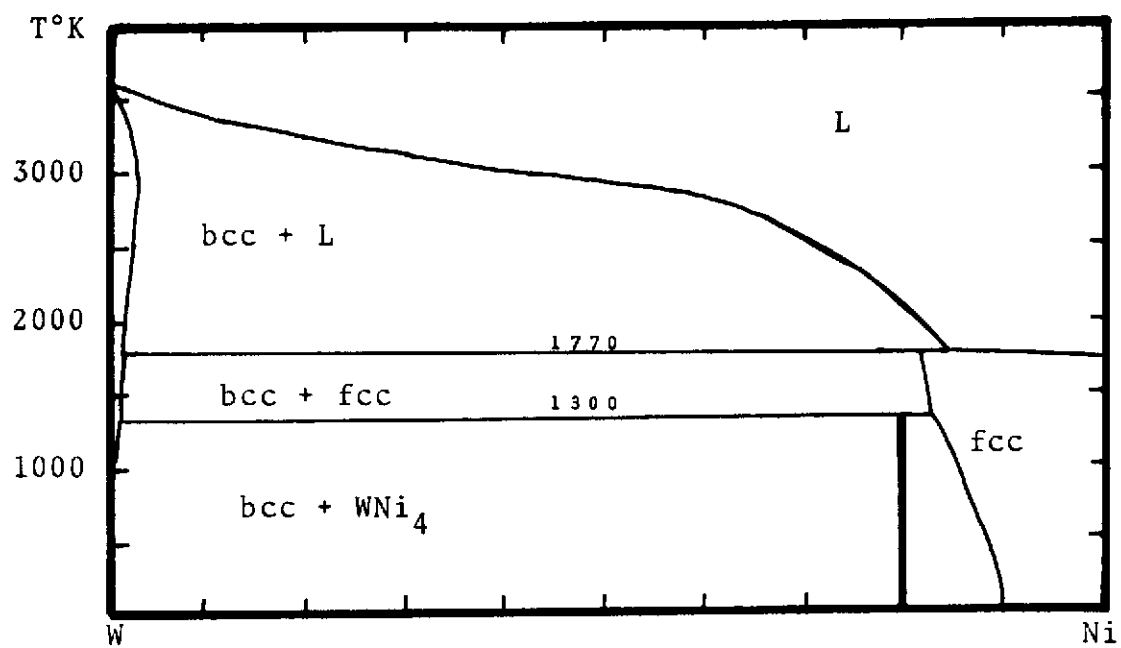


Figure 1. Calculated W-Ni Phase Diagram.

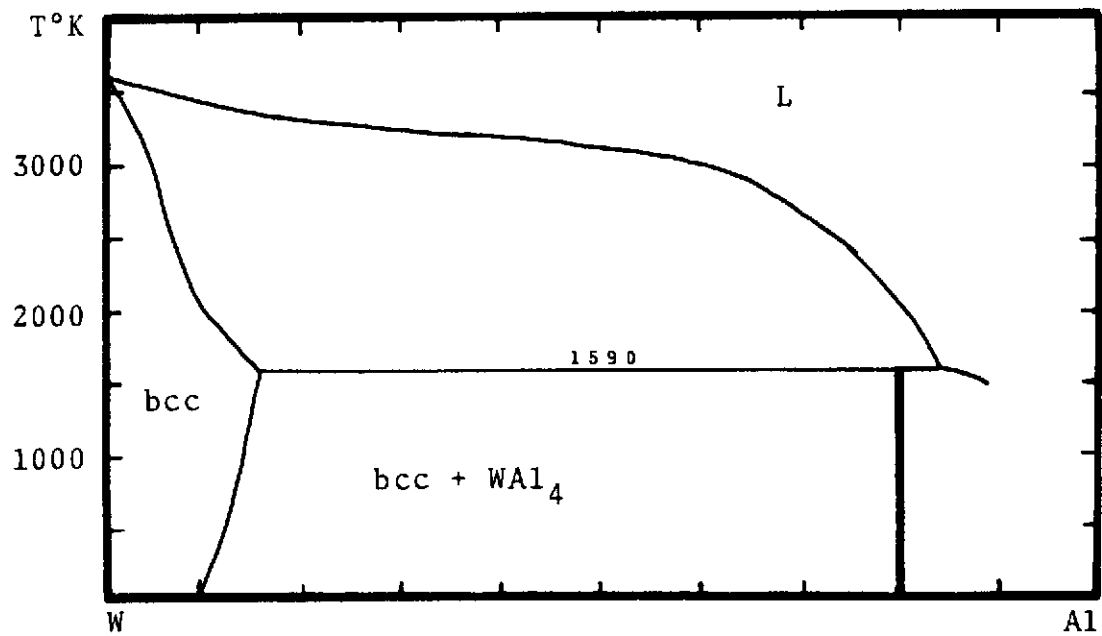


Figure 2. Calculated Partial W-Al Phase Diagram.

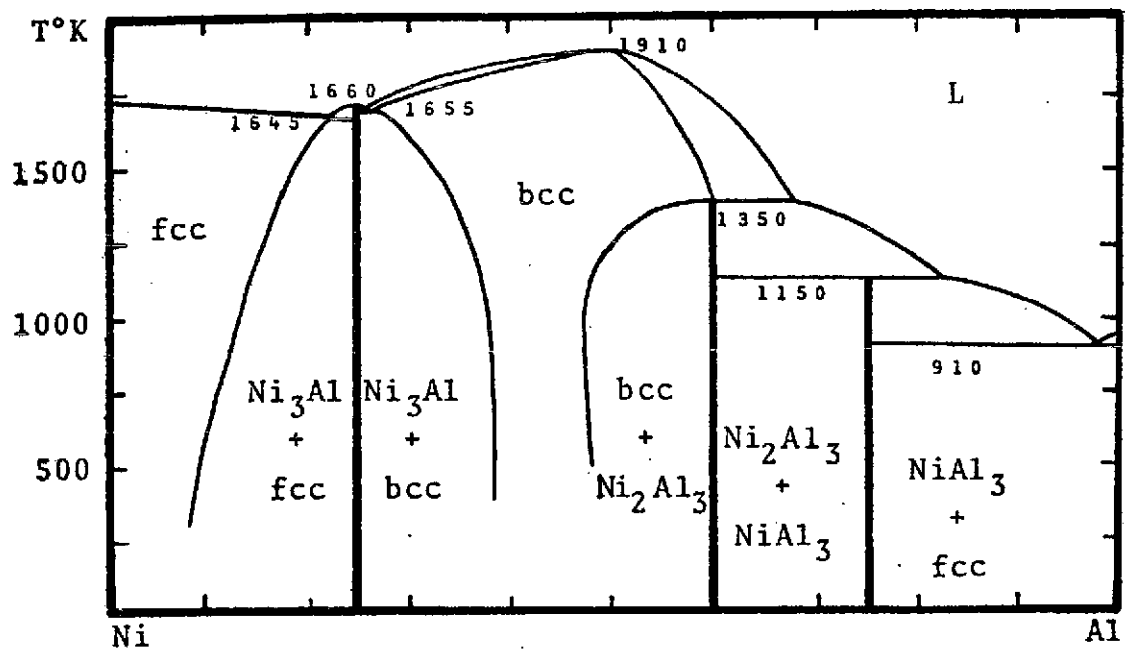


Figure 3. Calculated Ni-Al Phase Diagram.

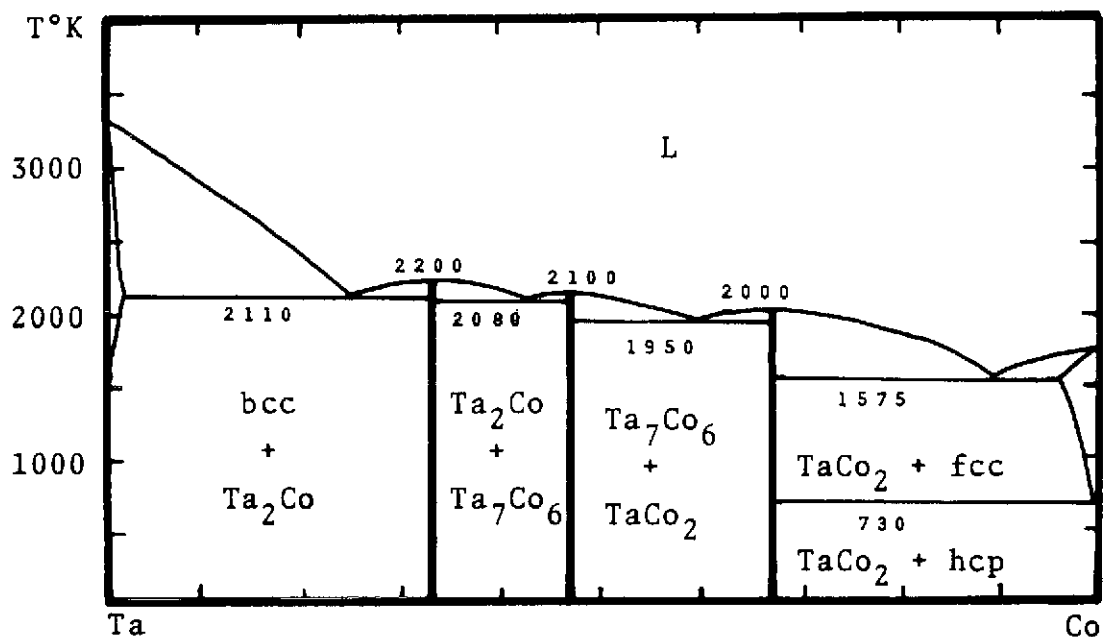


Figure 4. Calculated Ta-Co Phase Diagram.

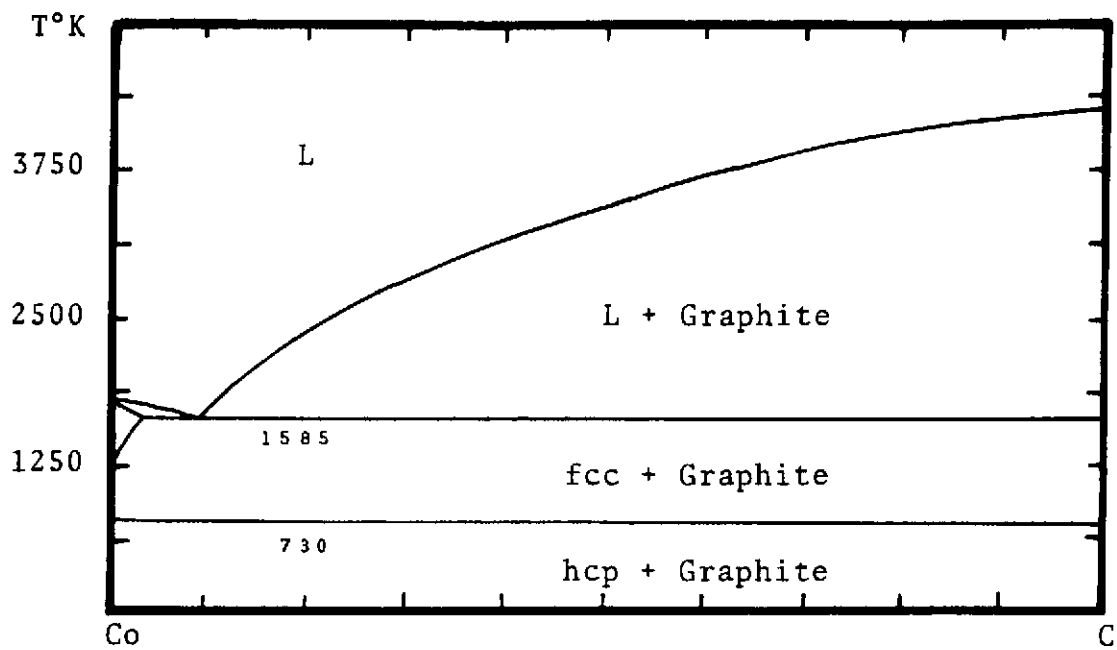


Figure 5. Calculated Co-C Phase Diagram.

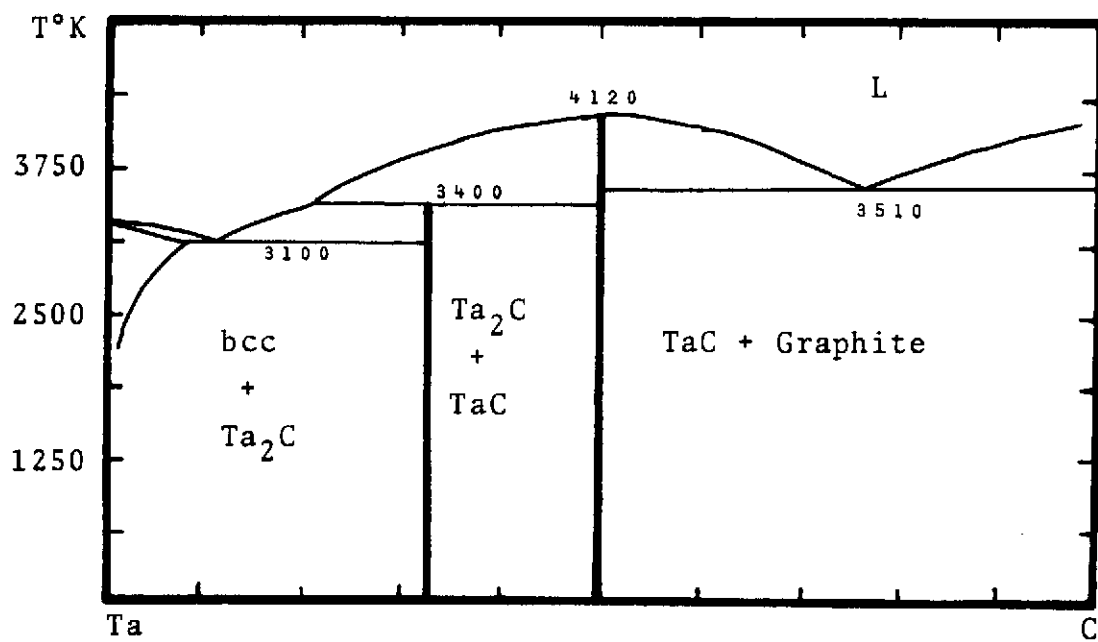


Figure 6. Calculated Ta-C Phase Diagram.

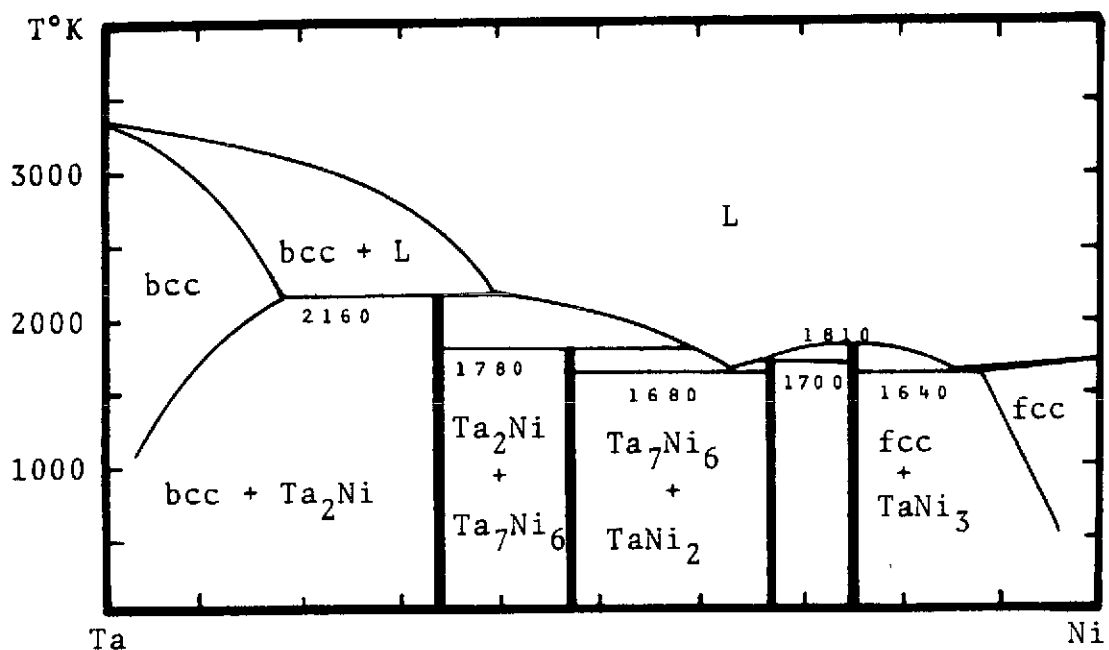


Figure 7. Calculated Ta-Ni Phase Diagram.

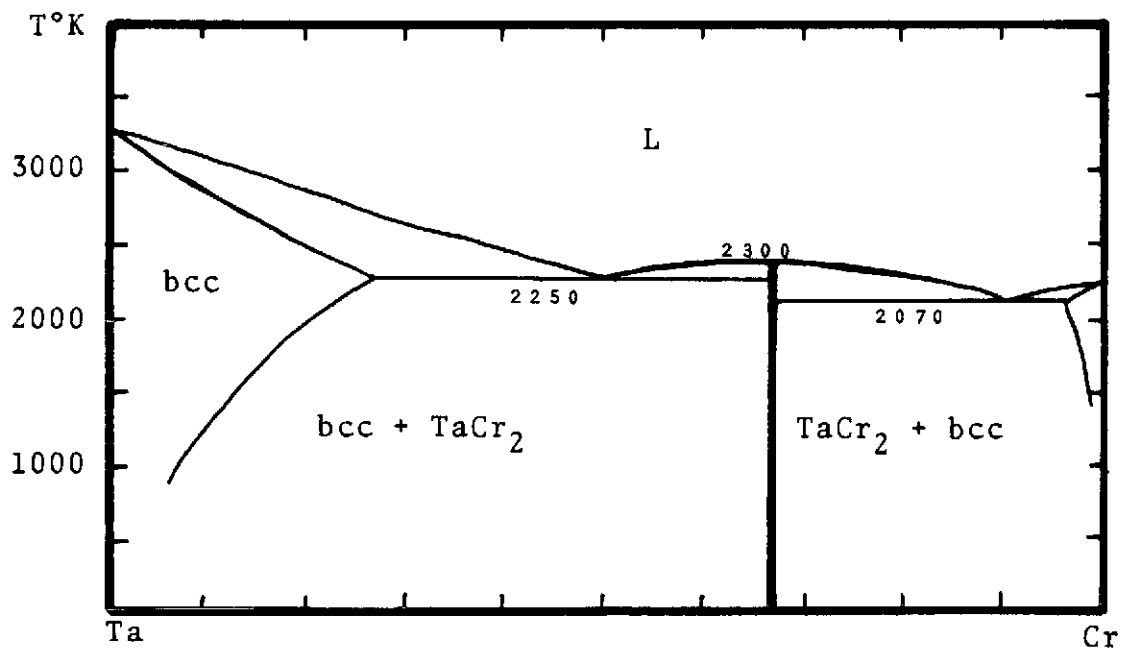


Figure 8. Calculated Ta-Cr Phase Diagram.

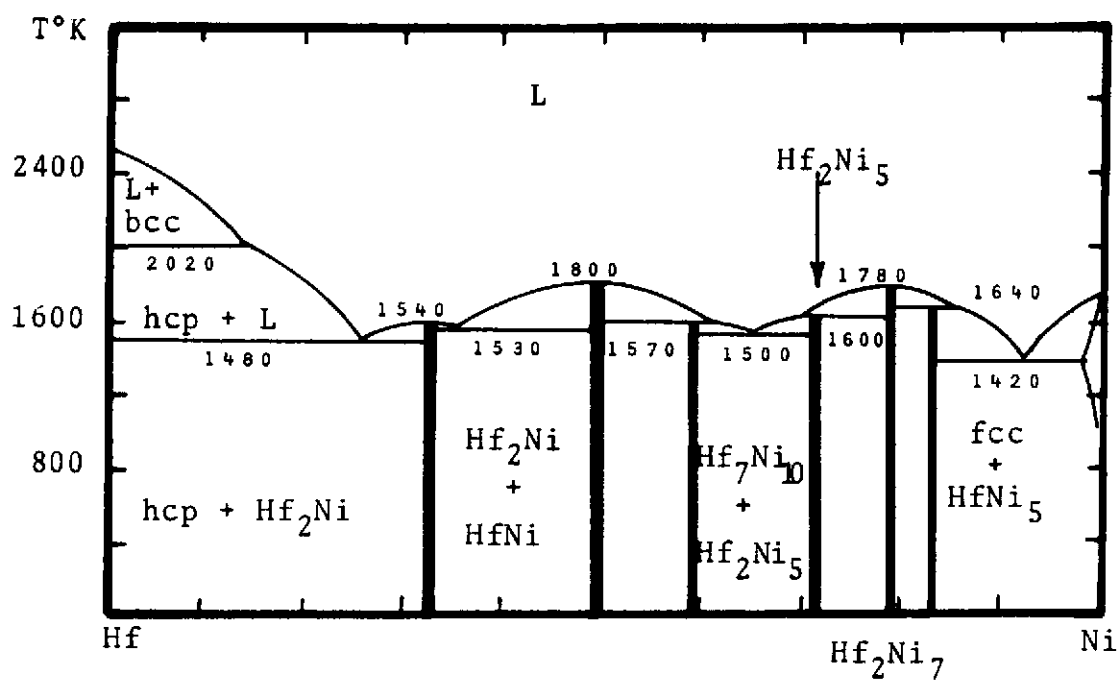


Figure 9. Calculated Hf-Ni Phase Diagram.

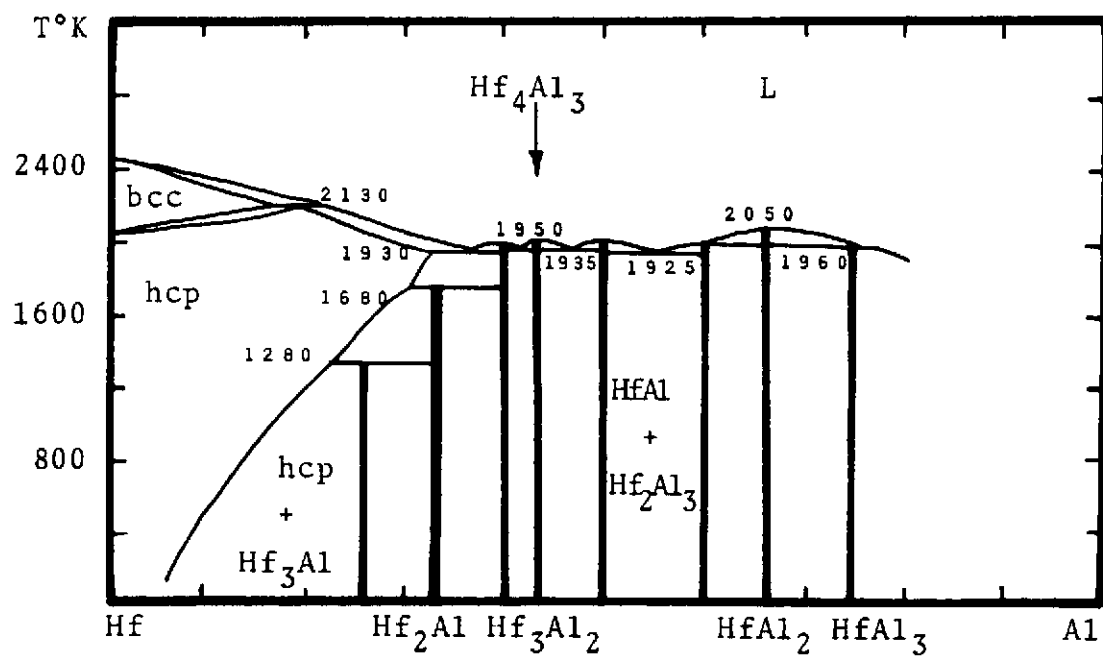


Figure 10. Calculated Partial Hf-Al Phase Diagram.

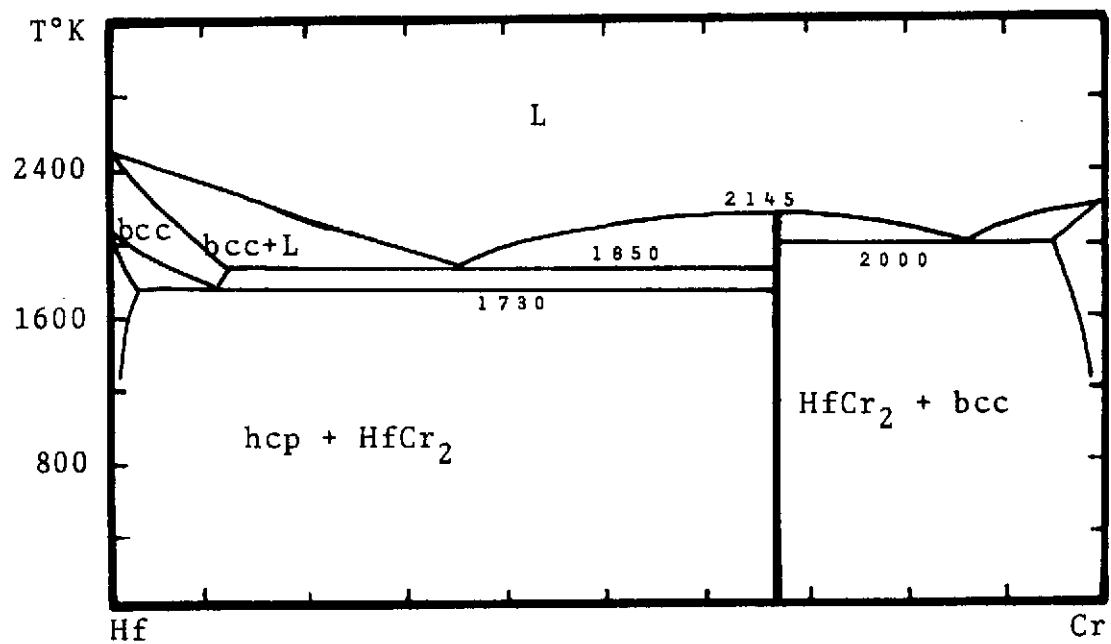


Figure 11. Calculated Hf-Cr Phase Diagram.

Liquidus
Projection

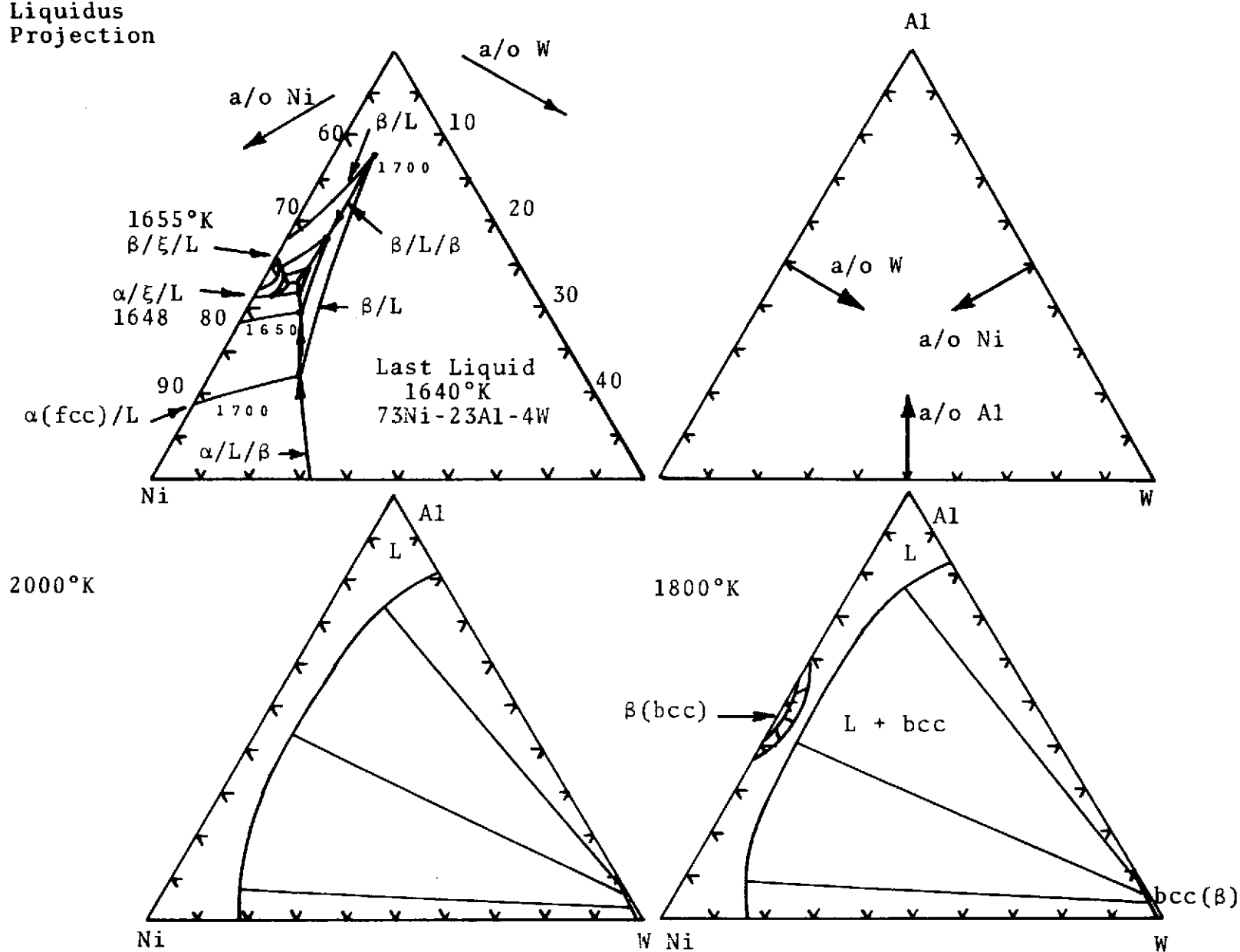


Figure 12. Calculated Liquidus Projection and Isothermal Sections in the Al-W-Ni System (Atomic Percent).

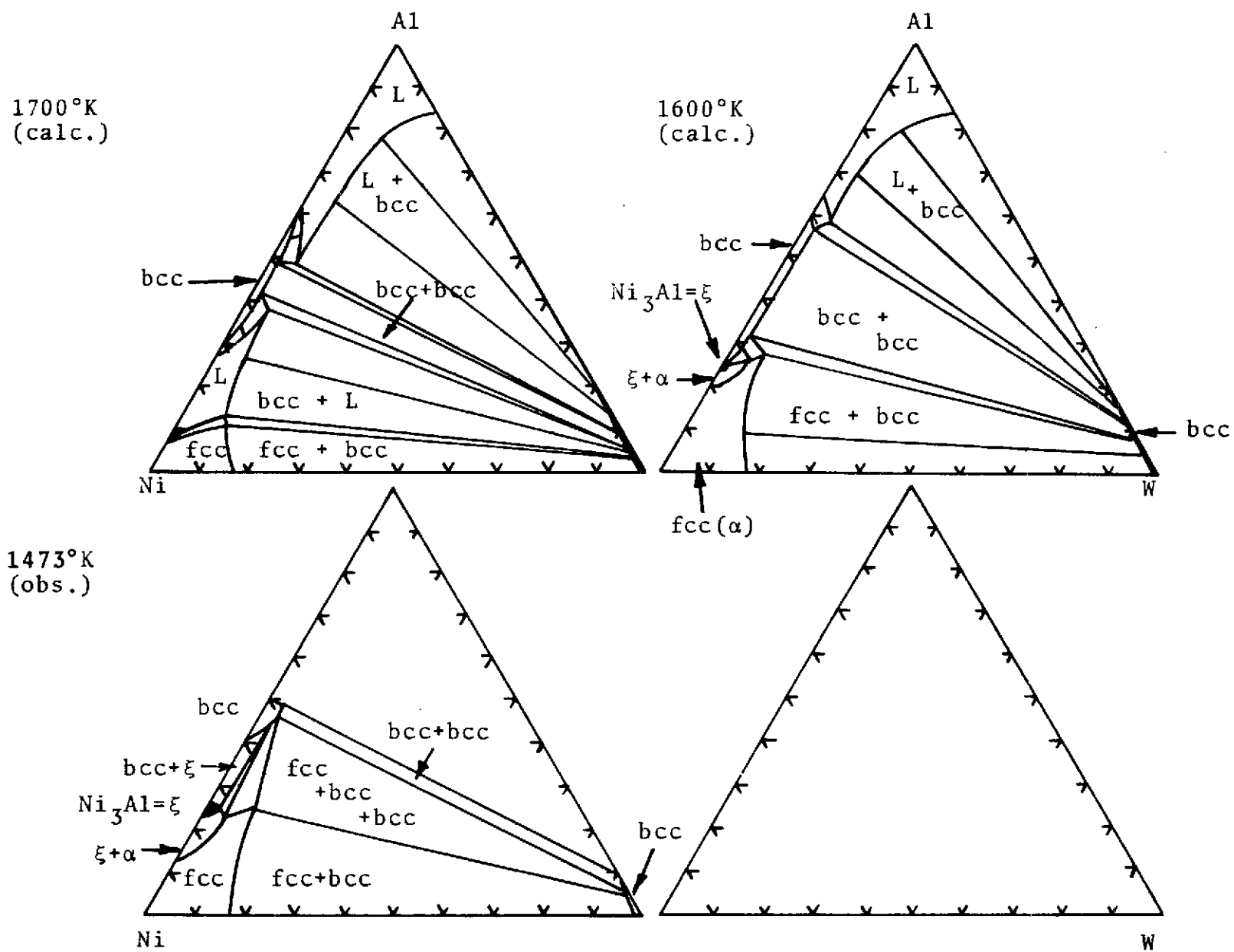


Figure 13. Calculated and Observed Isothermal Sections in the Al-W-Ni System (Atomic Percent).

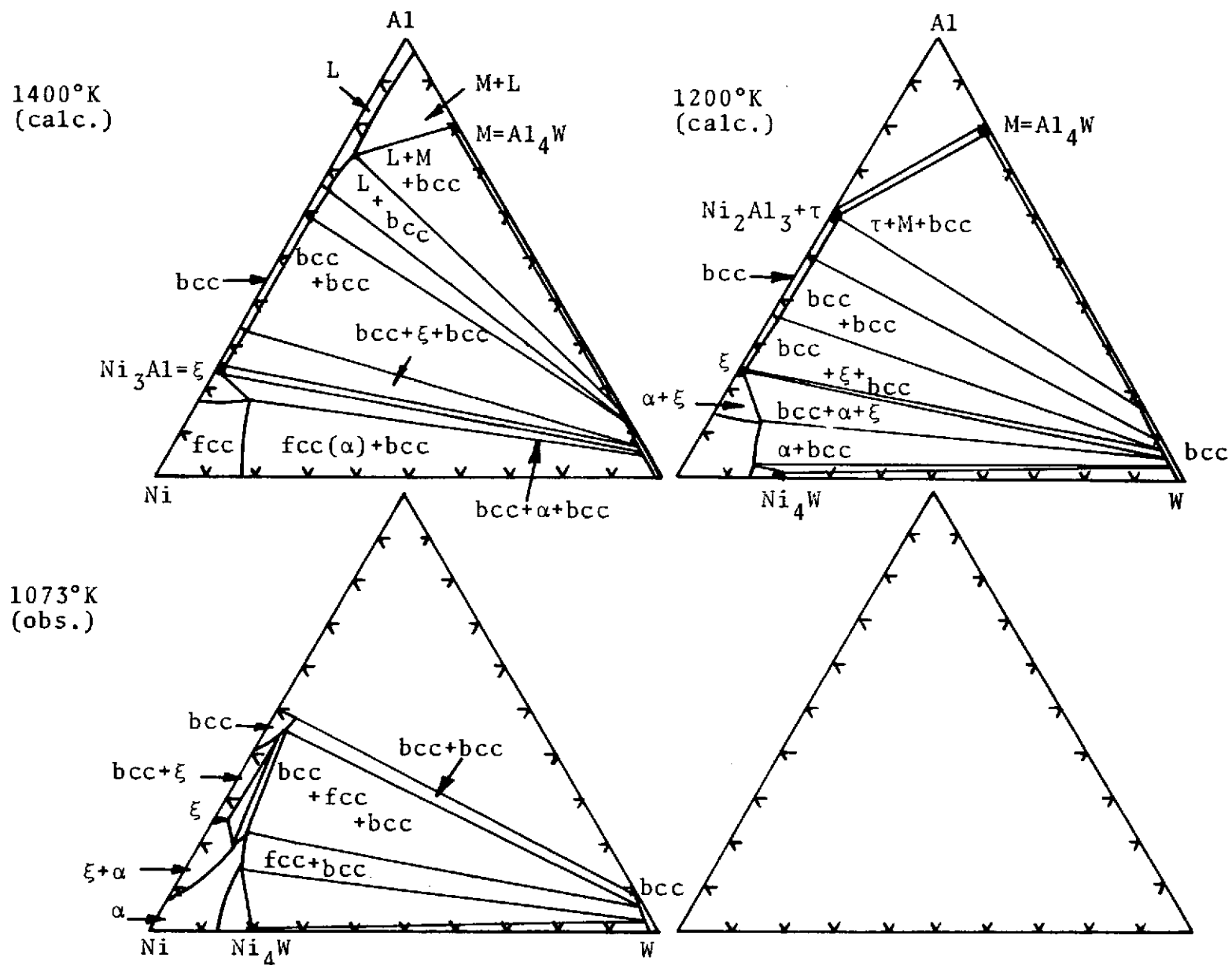
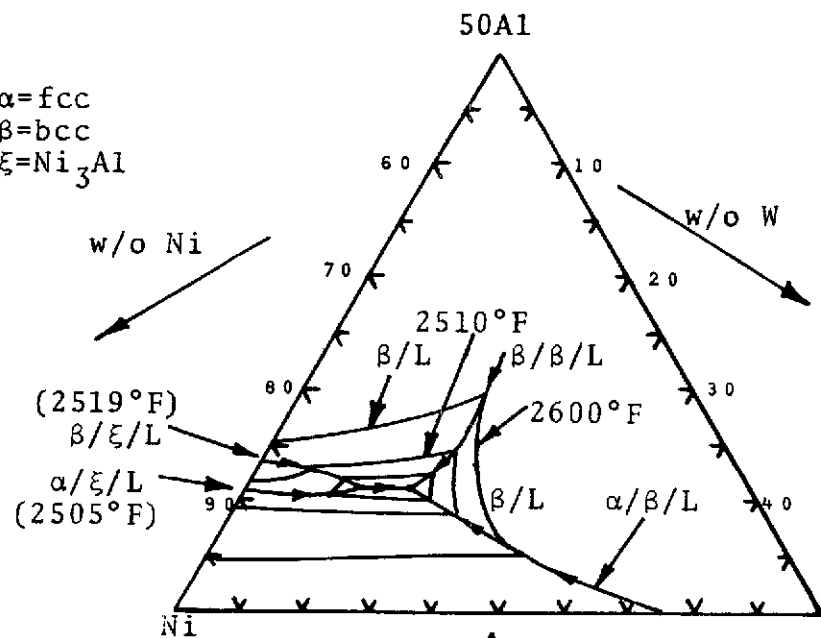


Figure 14. Calculated and Observed Isothermal Sections in the Al-W-Ni System (Atomic Percent).

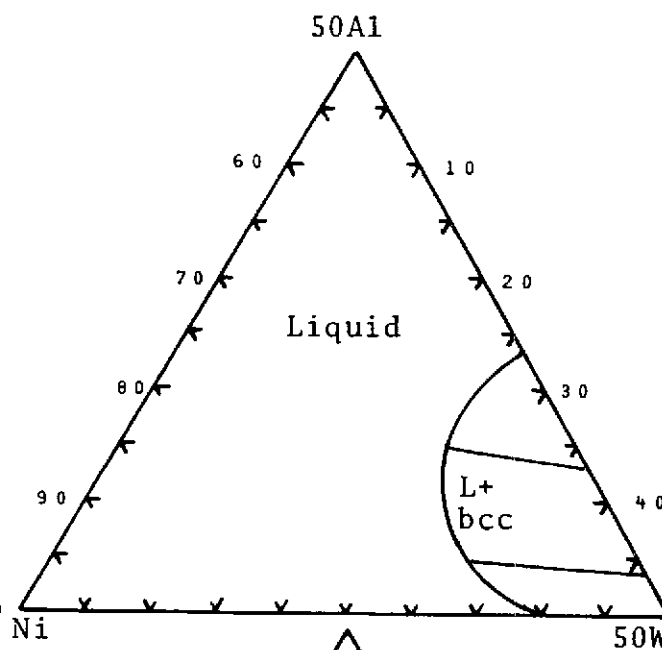
Liquidus Projection
Last Liquid 76Ni-11Al-13W
2492°F

α =fcc
 β =bcc
 ξ =Ni₃Al

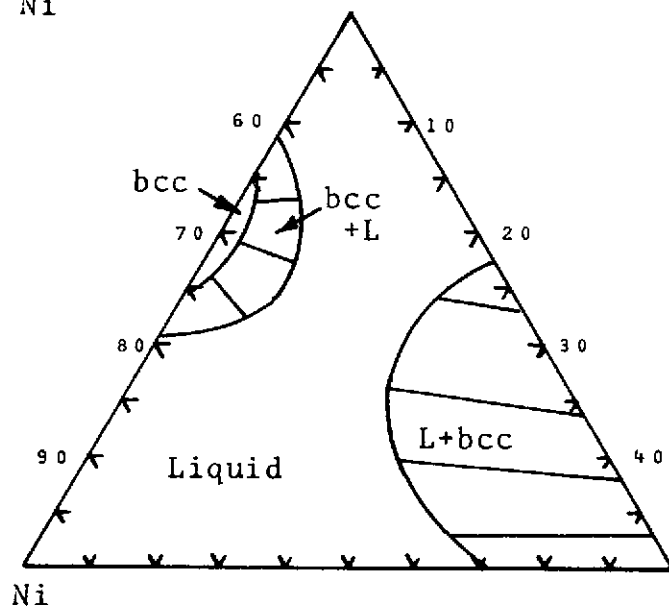
w/o Ni



2960°F



2780°F



2600°F

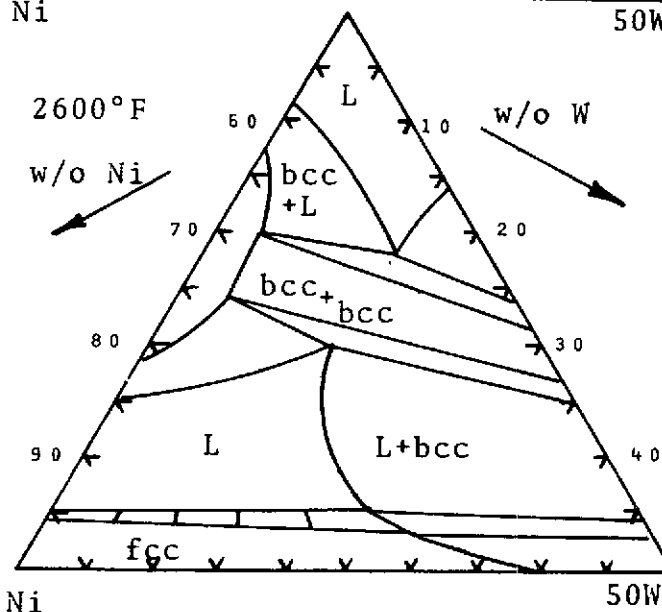
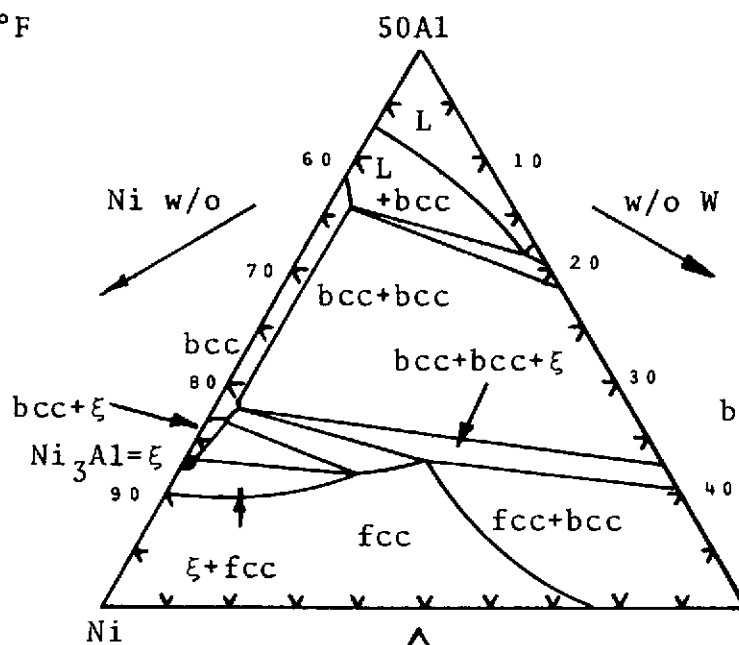
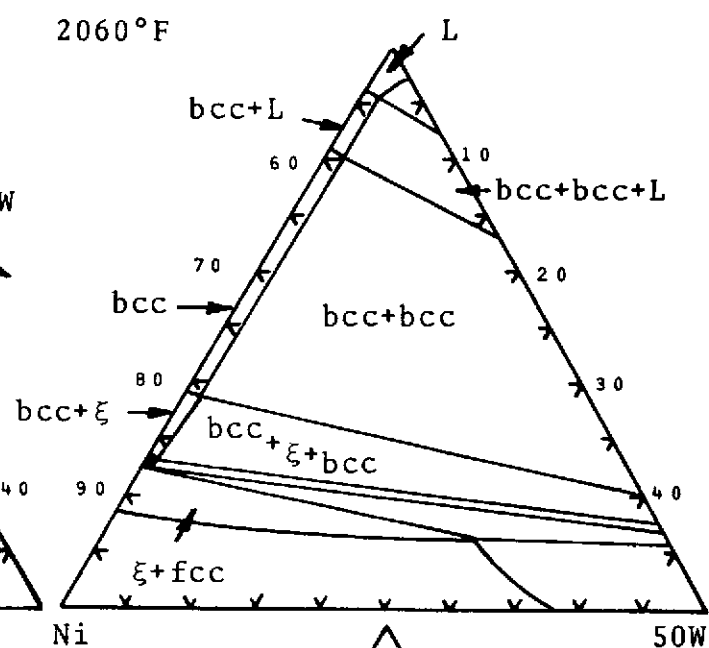


Figure 15. Calculated Liquidus Projection and Isothermal Sections in the Al-W-Ni System (Weight Percent).

2420°F



2060°F



1700°F

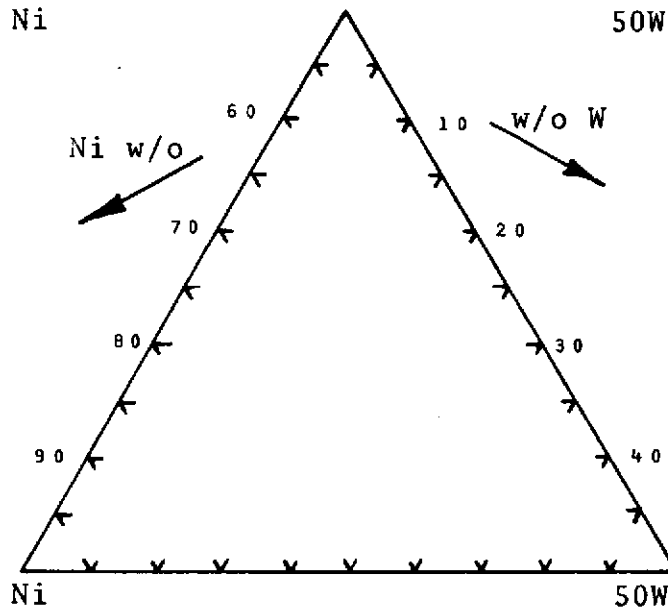
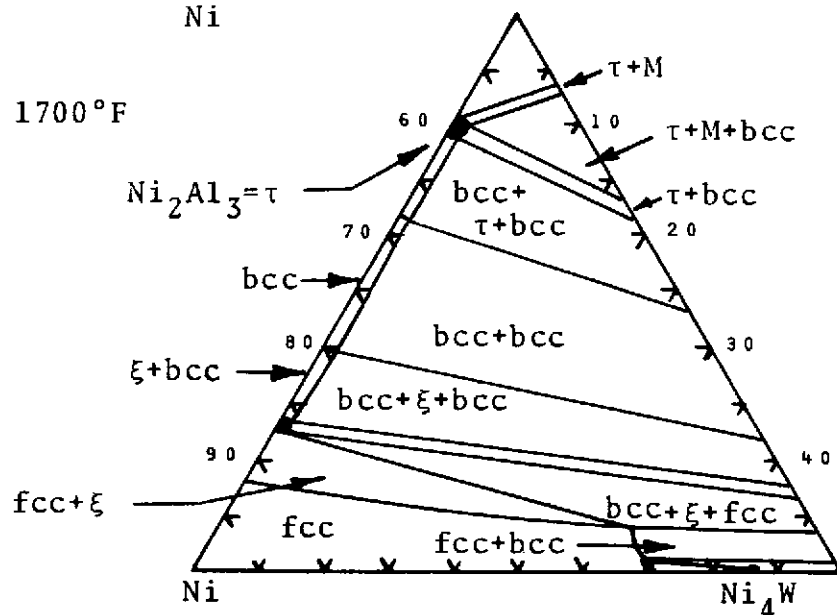


Figure 16. Calculated Isothermal Sections in the Al-W-Ni System (weight percent).

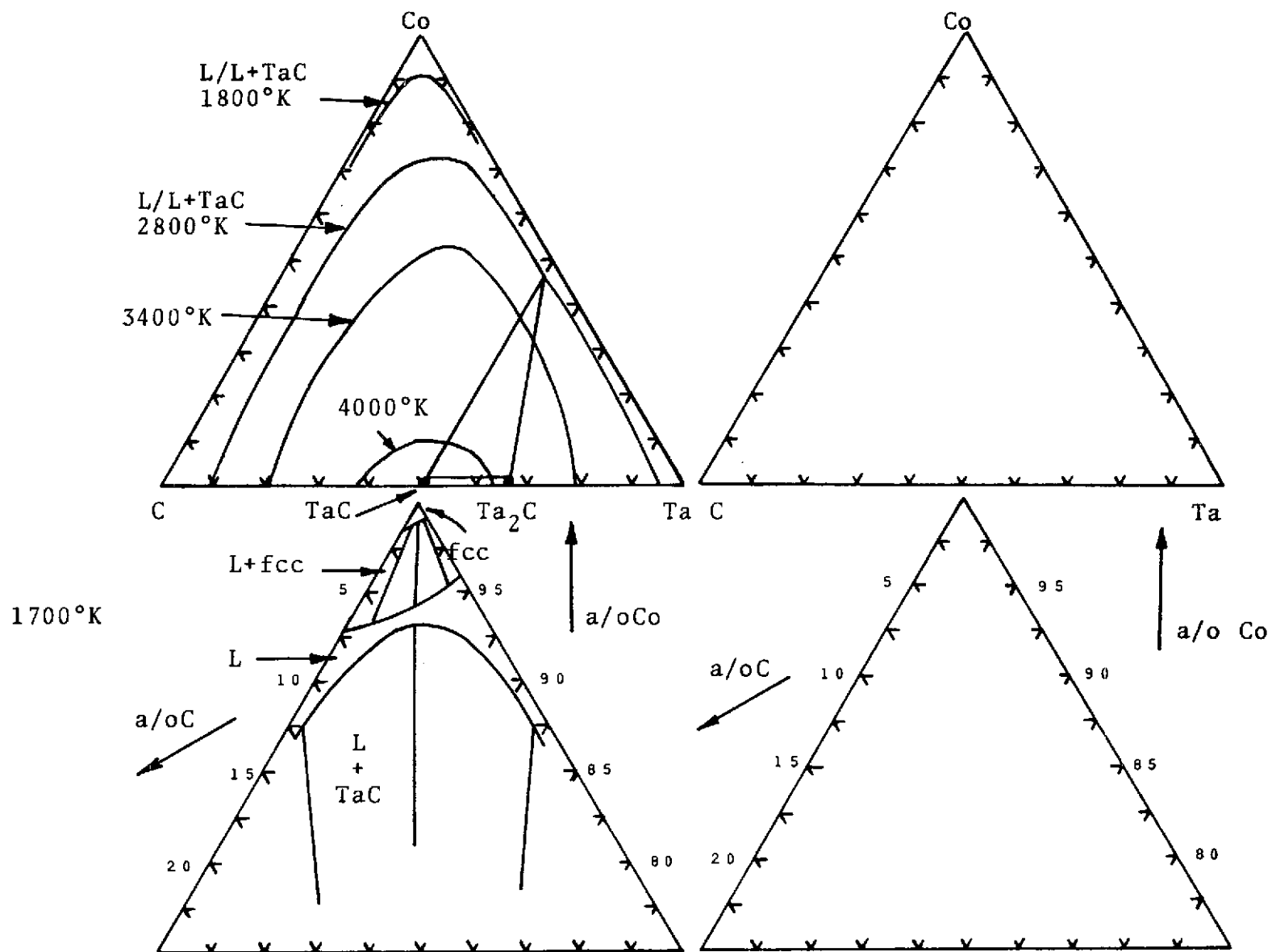


Figure 17. Calculated Partial Isothermal Sections in the Co-Ta-C System (atomic percent).

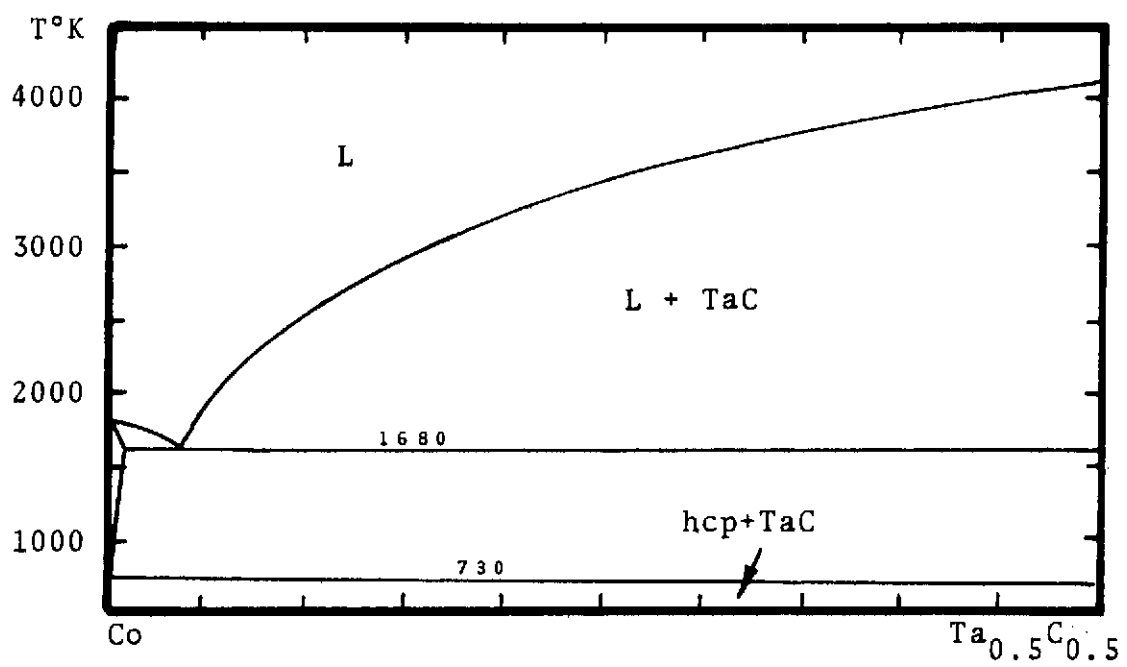


Figure 18. Calculated Co-TaC Quasi-binary Section.

Liquidus Projection

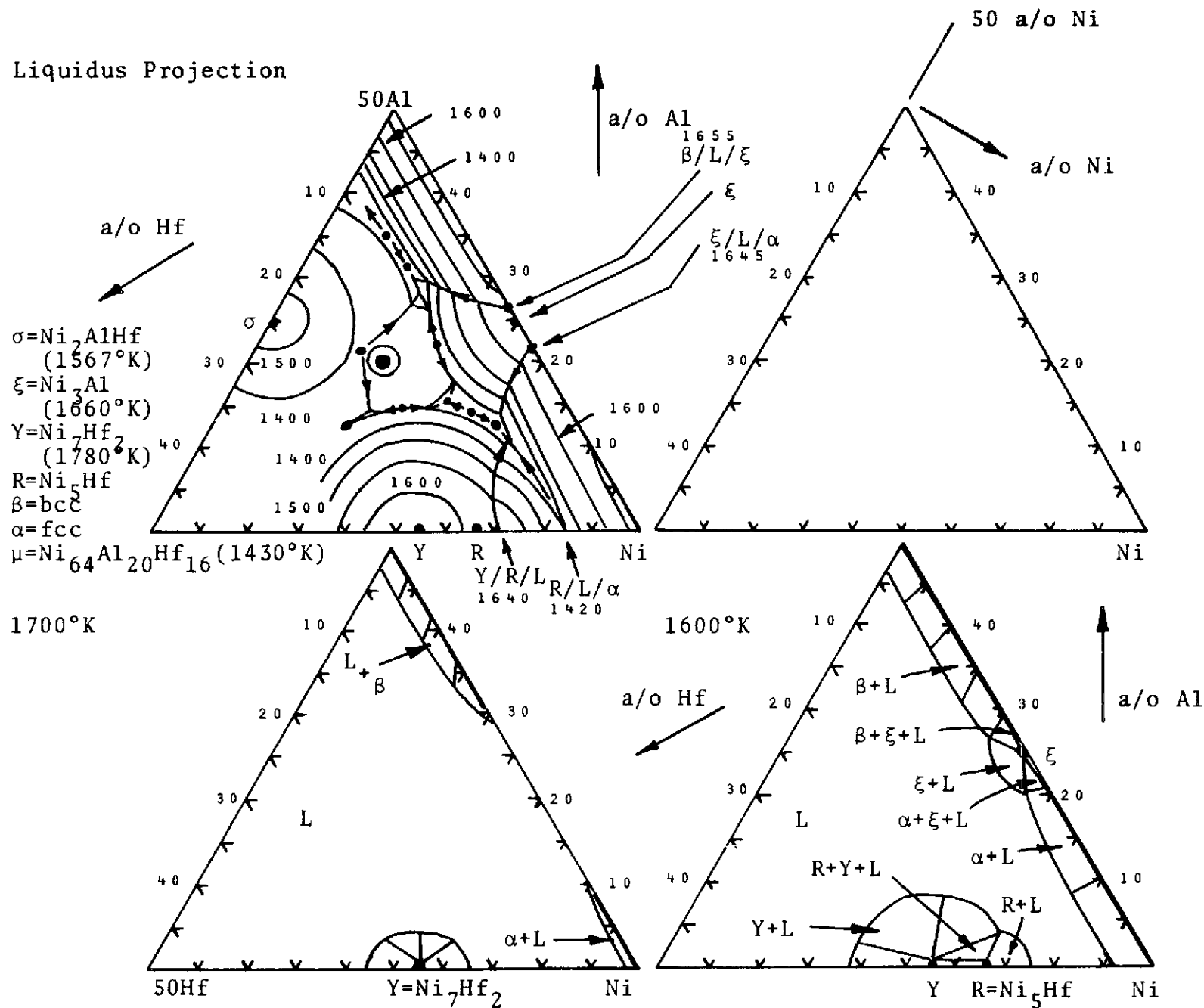


Figure 19. Calculated Liquidus Projection and Isothermal Sections in the Al-Ni-Hf System (atomic percent).

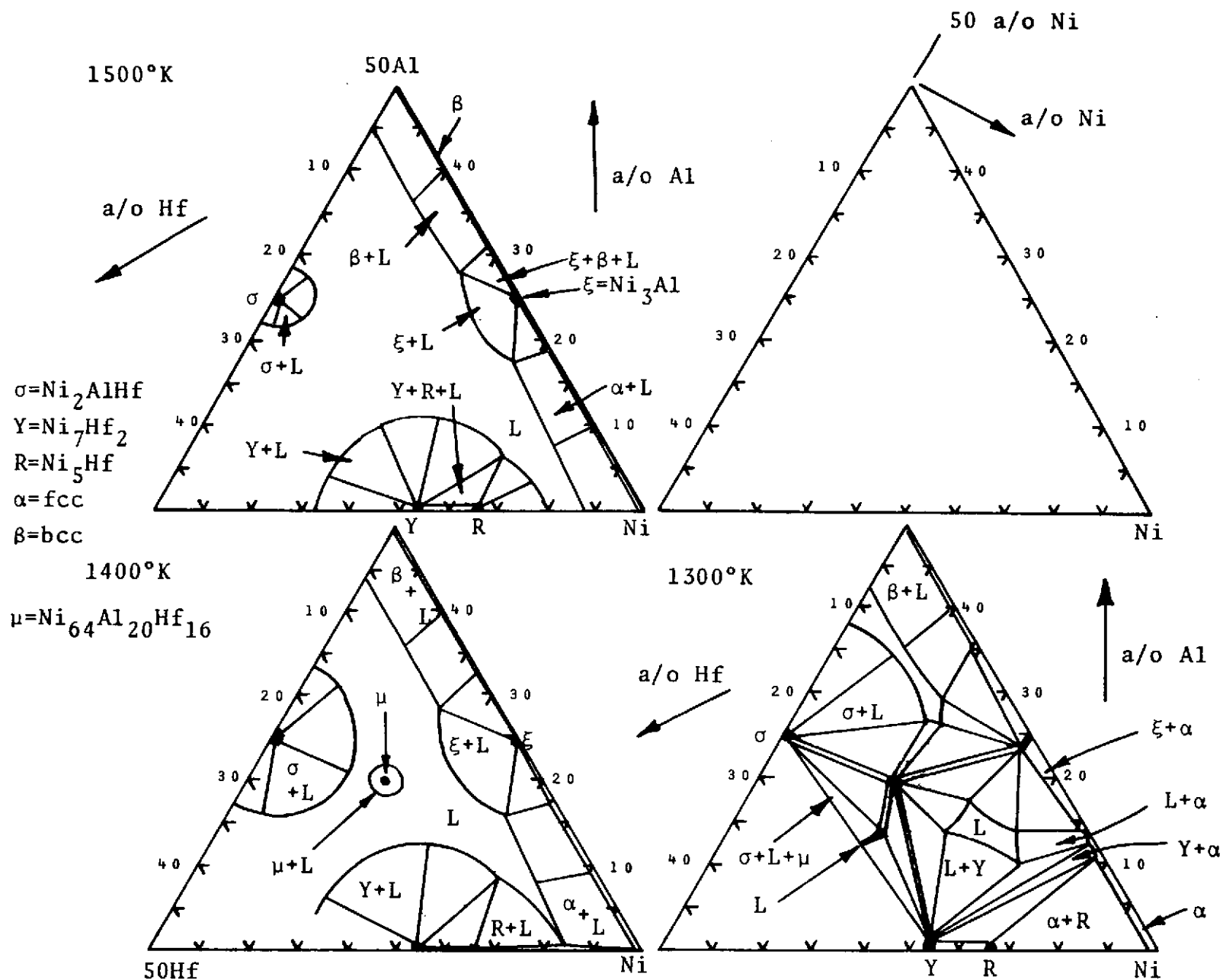


Figure 20. Calculated Isothermal Sections in the Al-Ni-Hf System (atomic percent).

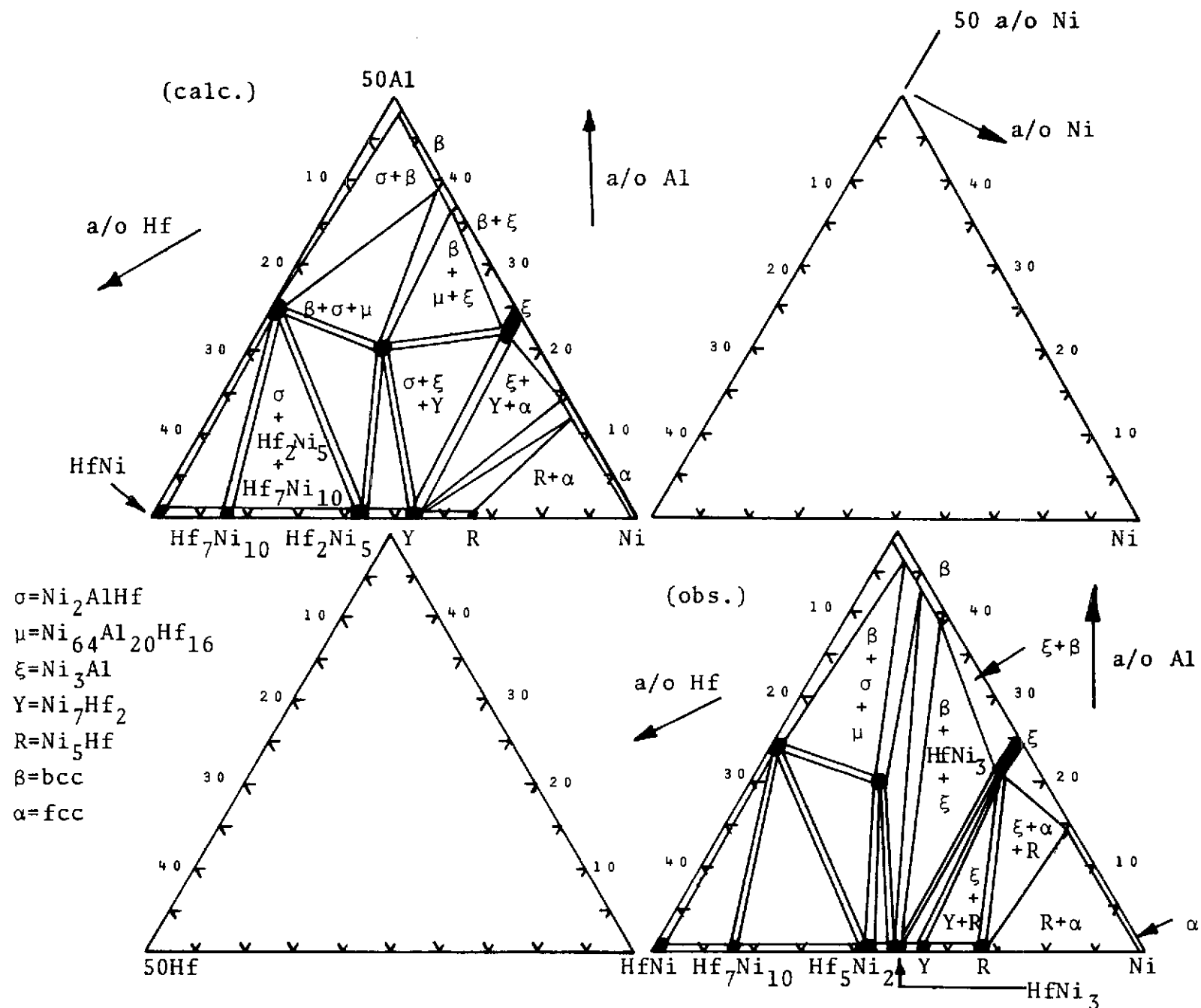


Figure 21. Calculated and Observed Isothermal Sections in the Al-Ni-Hf System at 1073°K (atomic percent).

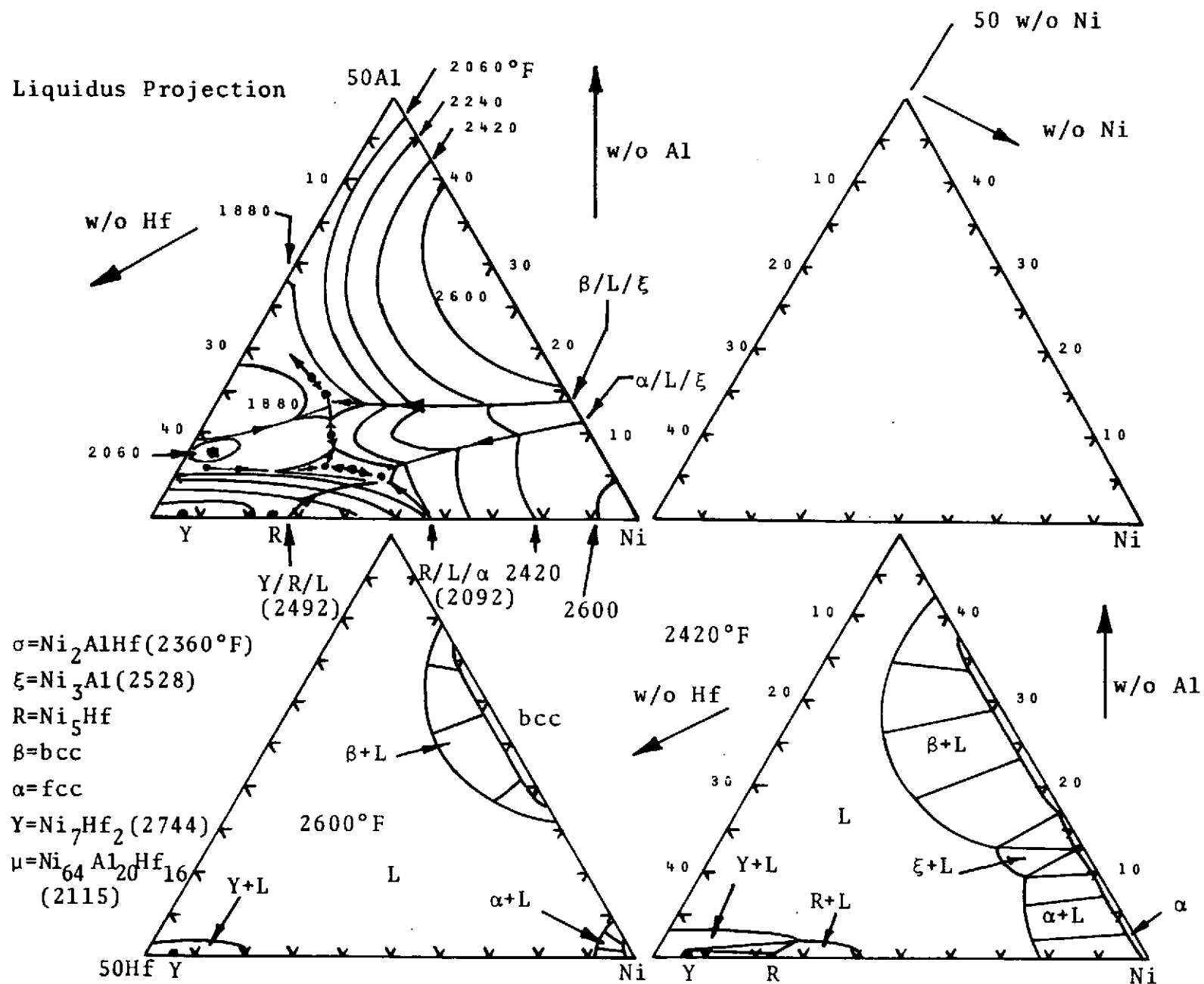


Figure 22. Calculated Liquidus Projection and Isothermal Sections in the Al-Ni-Hf System (weight percent).

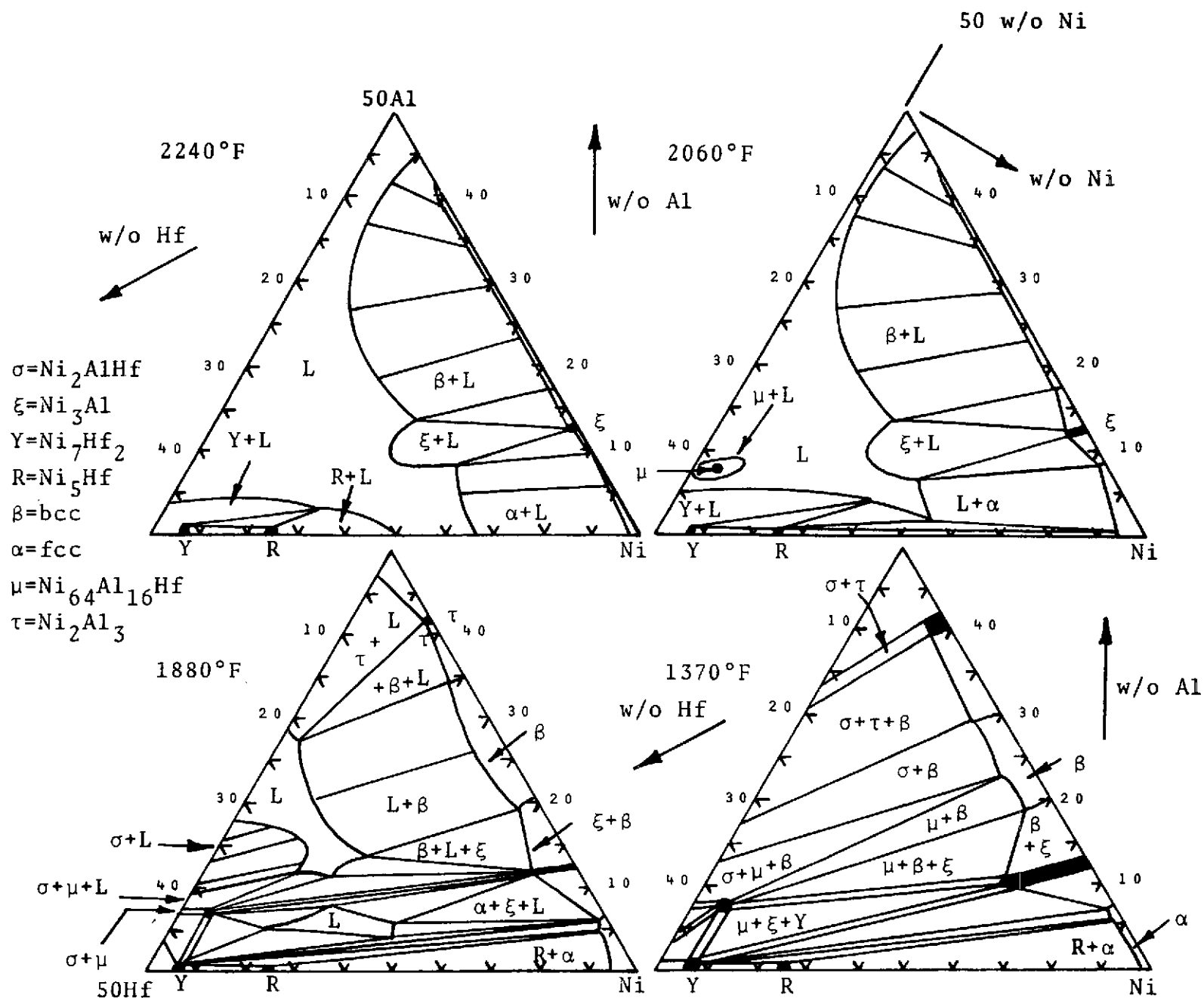


Figure 23. Calculated Isothermal Sections in the Al-Ni-Hf System (weight percent).

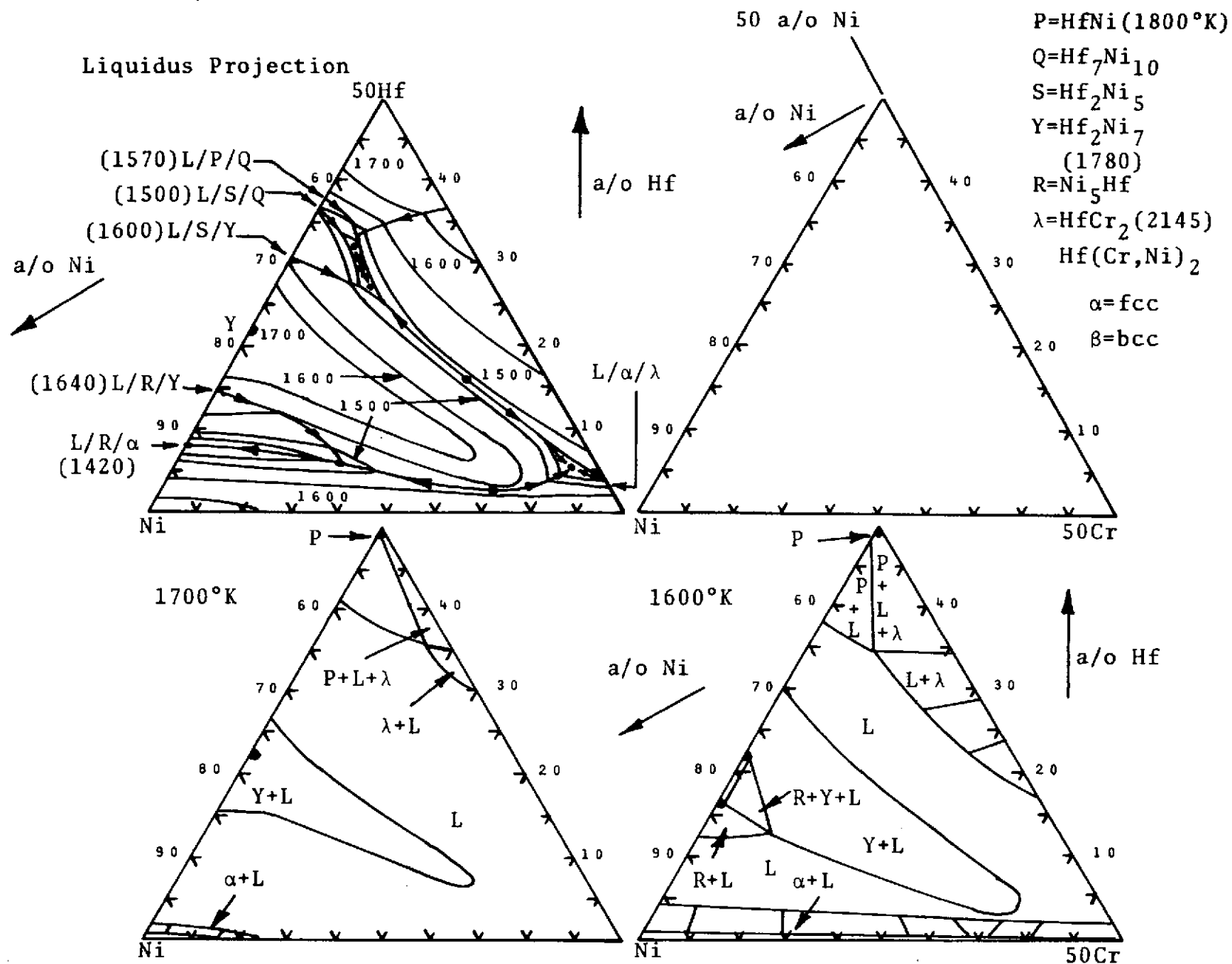


Figure 24. Calculated Liquidus Projection and Isothermal Sections in the Hf-Cr-Ni System (atomic percent).

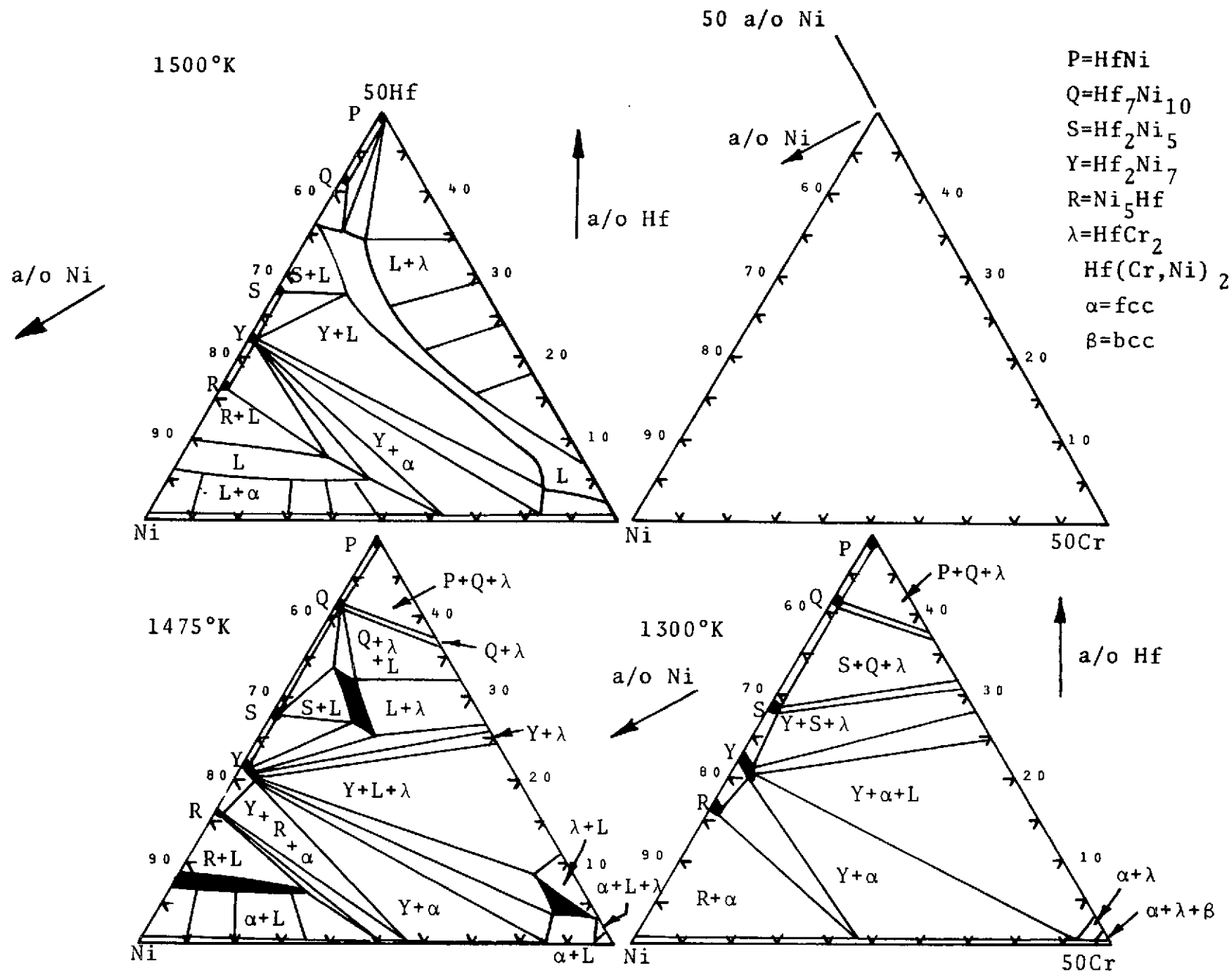


Figure 25. Calculated Isothermal Sections in the Hf-Cr-Ni System (atomic percent).

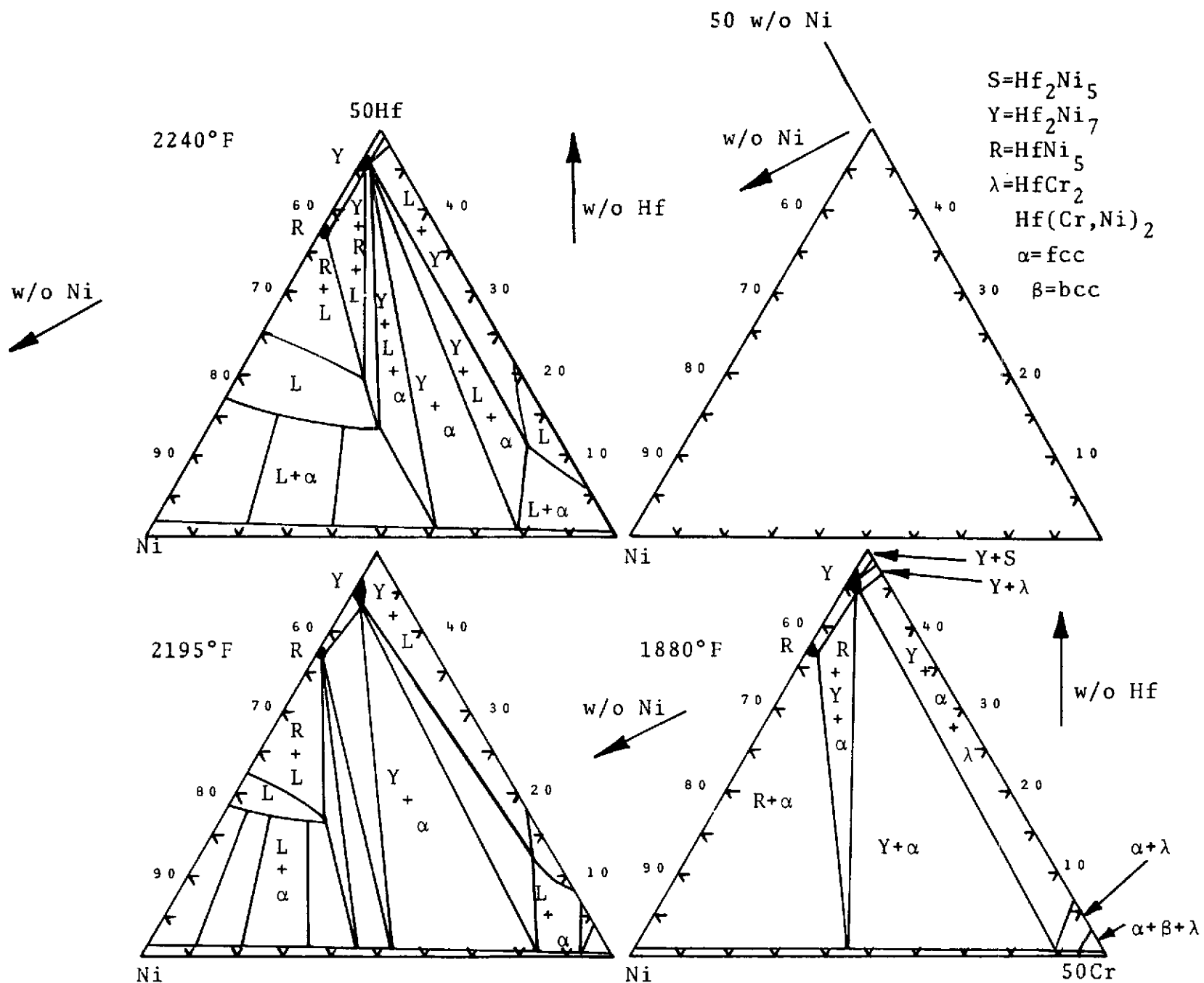


Figure 27. Calculated Isothermal Sections in the Hf-Cr-Ni System (weight percent).